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AUGUST 1950

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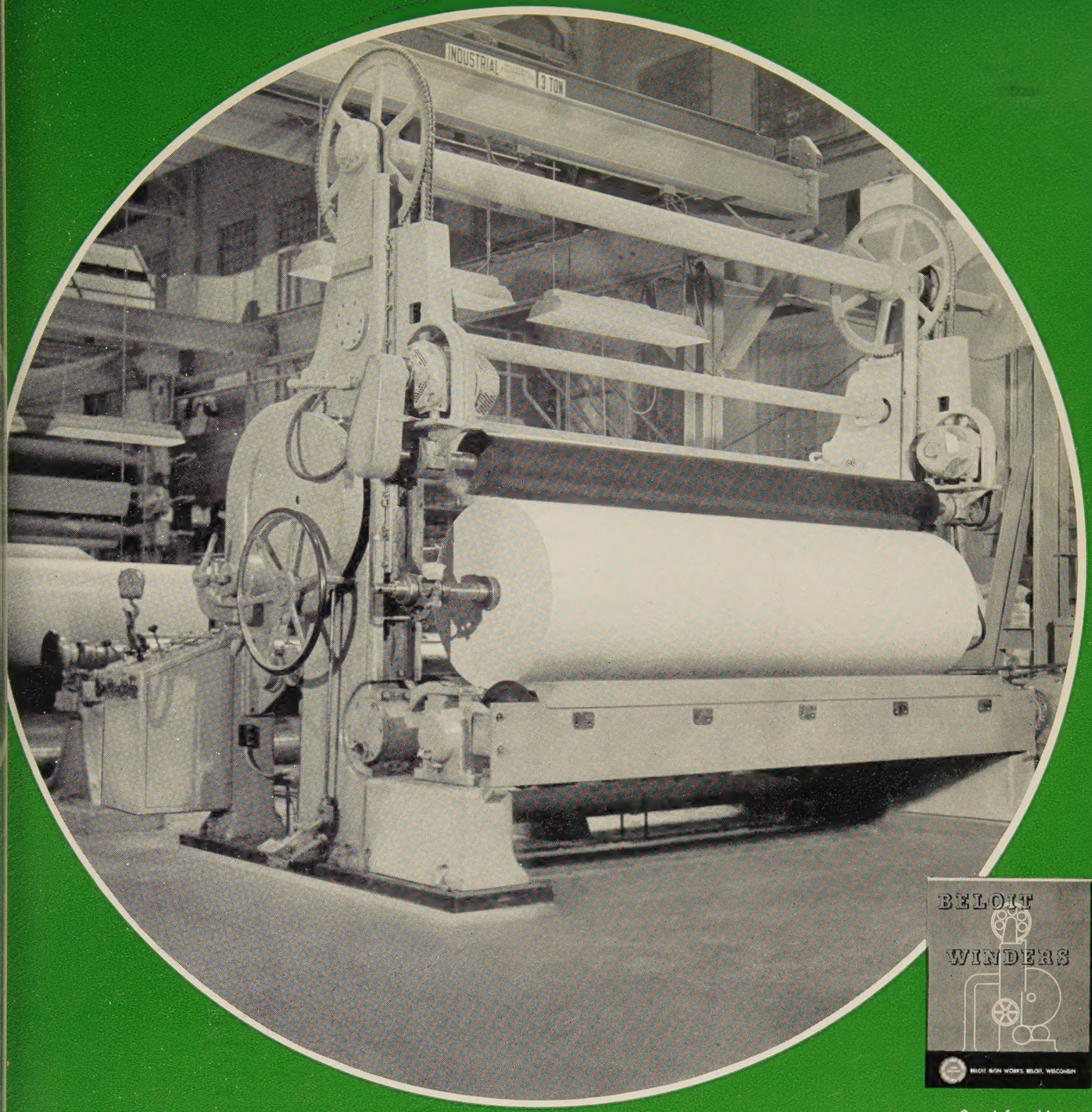

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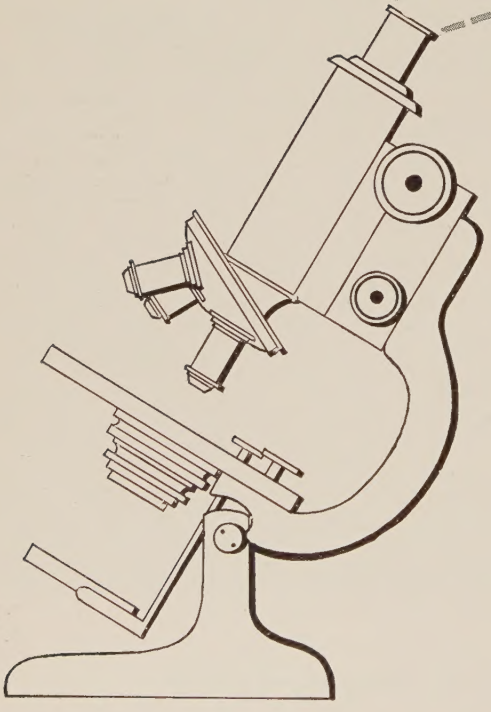

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Bucksport, Maine Mill	July, 1947	Continuous, Medium Consistency	Mixture of Sulfite & Groundwood—Spruce, Hemlock	Printing, Publication & Converting
Deferiet, N.Y. Mill	Jan., 1949	Multiple Chest, Low Consistency	Groundwood—Balsam, Spruce, Poplar	Coating Raw Stock
ESCANABA PAPER CO. Escanaba, Mich.	Aug., 1947	Continuous, Low Consistency	Groundwood—Spruce, Balsam, Poplar	Machine Coated Printing Papers & Mimeo
DIAMOND MATCH CO. Plattsburgh, N.Y.	Jan., 1948	Multiple Chest, Low Consistency	Groundwood—Spruce, Poplar	Tissue, Toweling & Napkins
BLANDIN PAPER CO. Grand Rapids, Minn.	March, 1948	Continuous, Medium Consistency	Groundwood—Spruce, Balsam, Poplar	Magazine & Printing Specialties
FINCH, PRUYN & CO., INC. Glens Falls, N.Y.	June, 1948	Continuous, Medium Consistency	Groundwood—Spruce, Balsam	Printing & Book Papers
ST. GEORGE PULP & PAPER CO., LTD. St. George, N.B. (Can.)	Nov., 1949	Continuous, Medium Consistency	Groundwood—Spruce	Market Pulp
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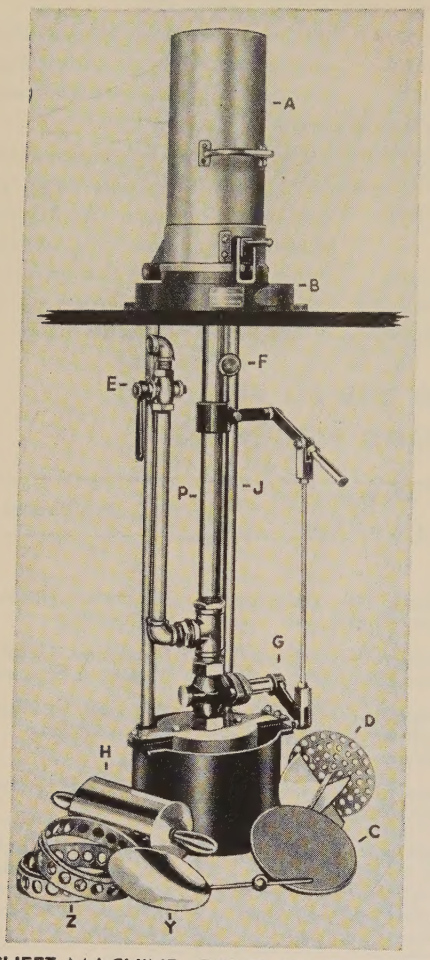

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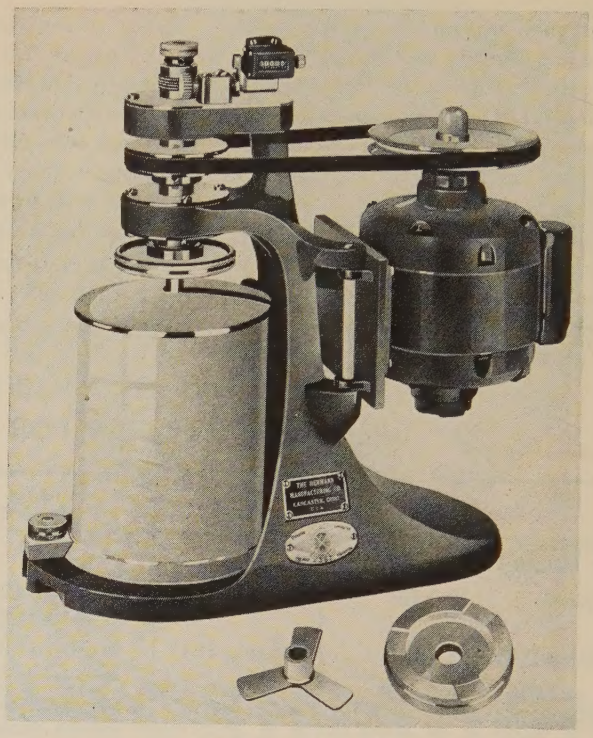

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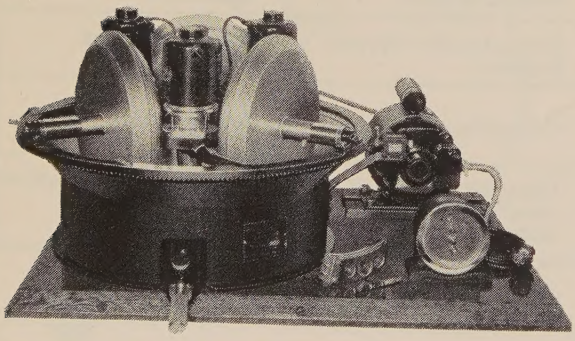

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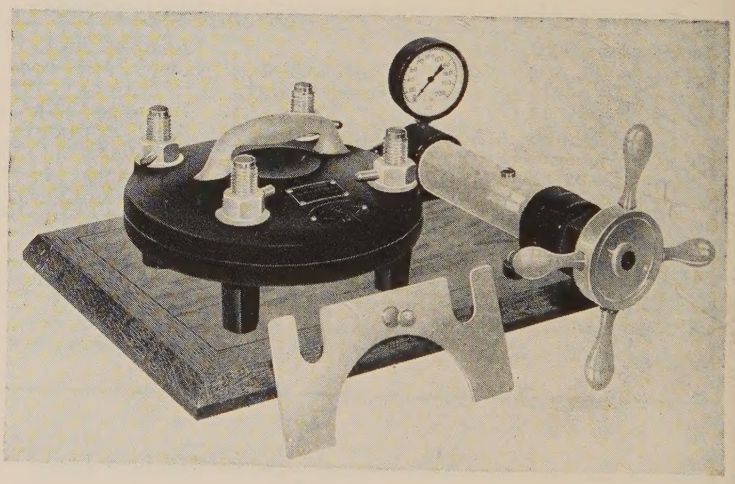

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Kraft Pulp Production

FREDERICK G. SAWYER, WALTER F. HOLZER, and LEONARD D. McGLOTHLIN

A NATION'S standard of living roughly parallels its consumption of pulp and paper. Each day every person in the United States uses almost 1 pound of paper (*9*), which is much more than is used in any other country. With yearly production about 30% that of steel by weight (*1, 10*), the size of the industry is impressive. Even more impressive is the important role played by chemistry and chemical engineering in making pulp and paper.

It all began several thousand years ago when glued strips of papyrus replaced cumbersome clay tablets as writing mediums. The Chinese later made paper from a mixture of bamboo fiber and old rags.

Chemistry actually entered the process only when wood became the cellulosic raw material. The problem was twofold: to remove most of the lignin binding the cellulose fibers in wood; and to retain the fibers with a minimum of degradation. At present this is accomplished in three chemical processes—soda, sulphite, and kraft (sulphate). The soda process uses sodium hydroxide to dissolve noncellulosic materials from the wood. The sulphite process attains similar ends with an acid cooking liquor. A mixture of sodium hydroxide and sodium sulphide is used to make kraft pulp (Table I).

Table I. Process and Product Characteristics

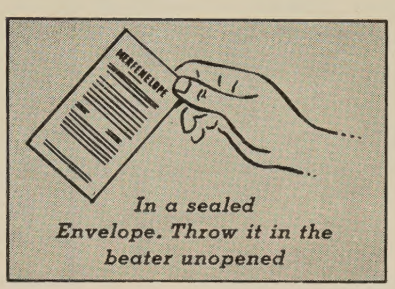
	Kraft	*Sulphite*	*Soda*
Cellulosic raw material	Almost any kind of wood, hard and soft; Camas uses hemlock, Douglas-fir, and white fir; woods cooked separately but all blown into same tank	Wood should be of good color and must be free of certain hydroxy phenolic compounds such as pinosylvin in pine (*7*) and flavanone in Douglas-fir (*11*); Camas uses hemlock and white fir	Any wood that can be used in kraft; low yields and strength of this pulp limit its production to short-fibered hardwood pulps which are used as filler in book and magazine grades
Cooking liquor composition	A 12.5% solution of NaOH, Na_2S, and Na_2CO_3; typical analysis of solids: 58.6% NaOH, 27.1% Na_2S, 14.3% Na_2CO_3; dissolving action due to first two; carbonate is inactive and represents the equilibrium residue between lime and Na_2CO_3 in the formation of NaOH	7% by weight SO_2, of which 4.5% is combined as sulphurous acid and 2.5% as calcium bisulphite; cooking 1 ton of pulp requires 225 to 300 pounds of sulphur and 350 to 400 pounds of lime rock	12.5% solution of NaOH and Na_2CO_3 in the ratio 85:15; dissolving action due solely to NaOH
Cooking conditions	Time: 2–5 hours; temperature: 340–355°F.; pressure: 100–125 p.s.i.	Time: 7–12 hours; temperature: 265–300°F.; pressure: 70–90 p.s.i.	Time: 6–8 hours; temperature: 330–340°F.; pressure 90–105 p.s.i.
Chemical recovery	Chemicals too expensive to discard; therefore, most of process is devoted to recovery of cooking chemicals with incidental recovery of heat through burning liquor organic matter dissolved from wood; chemical losses from system are replenished with salt cake, Na_2SO_4	SO_2 relief gas recovered; liquor discarded after wood digestion and pulp washing; no present salvage of chemicals but use of waste liquor being extensively studied	Sodium hydroxide recovered and reused as in kraft process, but make-up chemical is Na_2CO_3 instead of Na_2SO_4
Materials of construction	Digesters, pipe lines, pumps, and tanks can be made of mild steel or iron because caustic liquor does not readily corrode them; however, for more severe service Camas uses stainless steels such as types 430 and 304	Acid liquor requires digester lining of acidproof brick; fittings of chrome-nickel steels (Type 316), lead, and bronze	Same as kraft materials
Pulp characteristics	Brown color; difficult to bleach; strong fibers; resistant to mechanical refining	Dull white color; easily bleached; fibers weaker than kraft	Brown color; easily bleached; fibers weaker than kraft or sulphite
Typical paper products	Strong brown bag and wrapping: multiwall bags, gumming paper, building paper; strong white papers from bleached kraft, paper boards such as used for cartons, containers, milk bottles, and corrugated	White grades: book paper, bread wrap, fruit tissue, sanitary tissue	Usually blended with other pulps; book and magazine grades, coated papers, sanitary tissue

During the latter part of the nineteenth century, much salt cake (sodium sulphate) was available as a byproduct from the manufacture of hydrochloric acid. The German chemist, Dahl, found a new use for this salt cake when he invented the kraft process in 1889. Kraft means "strong" in German, an apt description of that kind of pulp or paper. Small quantities of it were made in Germany and Sweden before 1900. The first kraft mill in North America was located in East Angus, Quebec, in 1908.

FREDERICK G. SAWYER, Associate Editor, *Industrial and Engineering Chemistry*, Washington, D. C., WALTER F. HOLZER and LEONARD D. McGLOTHLIN, Crown Zellerbach Corp., Camas, Wash.

Merfenelopes

FOR SLIME CONTROL



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The process developed rapidly, especially in areas where large quantities of pine were available. This wood is not commonly pulped by the sulphite treatment because the heartwood contains pinosylvin (3,5-dioxystilbene) and its monomethyl ether which prevent digestion of the wood by acid liquor (*2*). Pine is readily pulped by alkaline kraft liquor. Large stands of southern pine in Alabama, Arkansas, Louisiana, Georgia, and Florida became the raw material for growth of a large kraft industry in those states.

Another great timber area of the United States is the Pacific Northwest. Until recently, large stands of Douglas-fir were untapped for pulp because the wood resists sulphite pulping. This is due to low permeability and the presence of certain phenols—for example, taxifolin, a flavanone—which form insoluble lignin compounds (*7*).

It was not until World War II that Douglas-fir was pulped by the kraft process in regular and substantial quantities. This represented culmination of plans begun in 1925 when the Crown Zellerbach Corporation built a kraft mill at Camas, Wash., on the Columbia River. At present this mill is one of the nation's largest in total production with its daily capacity of 360 tons of kraft pulp (averaging 38% Douglas-fir, with as much as 65% in some grades), 350 tons of sulphite pulp, and 30 to 35 tons of groundwood.

In general, kraft pulp goes into wrapping and bag paper, shipping cases, and other papers where high strength must be combined with low cost. Four hundred different papers are made at Camas, Wash., although the accent is on lightweight tissue grades. This mill is the largest unit of seven pulp and paper mills comprising the parent Crown Zellerbach Corp. Others are located in West Linn, Ore., Lebanon, Ore., Port Townsend, Wash., Port Angeles, Wash., Ocean Falls, B. C., and Carthage, N. Y.

THE CAMAS MILL

The phenomenal growth of the kraft industry (Fig. 1) can be appreciated when it is realized that the Camas mill of the Crown Williamette Paper Co. (a division of Crown Zellerbach Corp.) produces ten times the entire kraft pulp output of the United States and Canada of 40 years ago. The present size of the industry by geographical areas is shown in Table II.

Table II. 1948 U. S. Kraft Pulp Production by Regions (*12*)

	Pulp (air-dry weight,)[a] tons				
	New England and Middle Atlantic	*Lake*	*Pacific*	*South*	*Total*
Bleached	84,227	49,449	82,959	822,053	1,038,688
Semibleached	0	43,769	36,872	148,700	229,341
Unbleached	93,785	219,934	377,698	4,065,776	4,757,193
Total	178,012	313,152	497,529	5,036,529	6,025,222

[a] As reported to U. S. Pulp Producers Assoc. by 98% of industry and estimated for 2%.

The Camas plant uses about 600,000 board feet (1200 cords) of pulpwood a day. To feed this voracious appetite and that of the other Crown Zellerbach mills, the company practices a program of sustained yield logging on 200,000 acres of forest land in Washington and 300,000 acres in Oregon. A small amount of additional wood must be bought to satisfy the total needs. The forest lands are located in several distinct areas. The rain forests of the Pacific Coast contain mostly western hemlock and Sitka spruce. On the west slope of the Cascade Mountains south and east of Oregon City, Ore., the predominant species is Douglas-fir. Both sides of the Columbia River have large stands of Douglas-fir. The Olympic Peninsula grows mainly western hemlock.

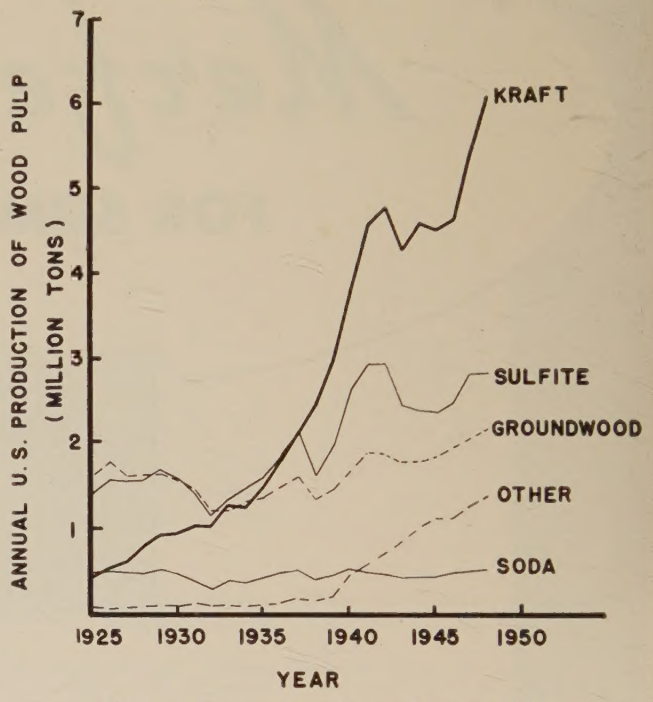
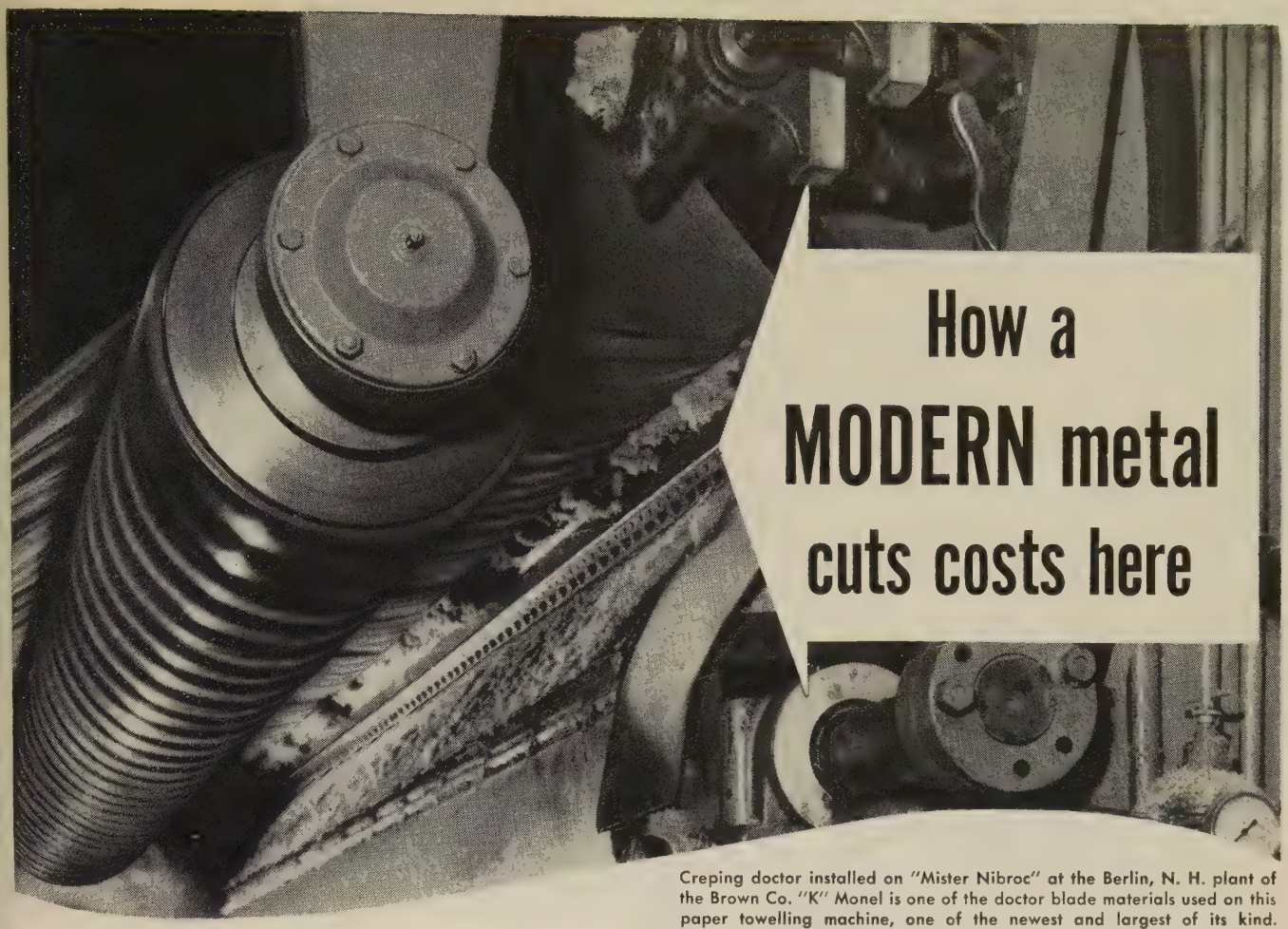


Fig. 1. Domestic pulp production (11)

These areas are being developed on a long-term basis. Roads through the forests are of the permanent type and are strategically located to allow access for fire protection. They enable loggers to get to any area for harvesting logs according to the plan best suited to that particular area. This may mean selective cutting by thinning or by clearing small blocks. Cutover land is being brought back to production by hand planting of seedlings and by helicopter broadcast of seeds. Although the latter is far cheaper, its use for only 3 years would make any statement on its success premature.

Forest rodents were found to eat large quantities of the tree seeds soon after their aerial distribution. It has been found necessary to do extensive poisoning prior to seeding. An area of poisoned grain several hundred yards wide surrounds the area to be seeded. Then the seeds are distributed. By the time the rodents have eaten their way through the poison barrier, the trees have sprouted and are safe from attack.

Using an average figure of 2 cords of wood (1000 board feet) per acre per year as the production of the land, it requires about 200,000 acres of forest to sustain the Camas mill. This does not allow for any natural catastrophe, insect damage, or fire. A 60-year growing cycle is calculated for pulpwood logs; sawmills use a 100-year cycle.



How a MODERN metal cuts costs here

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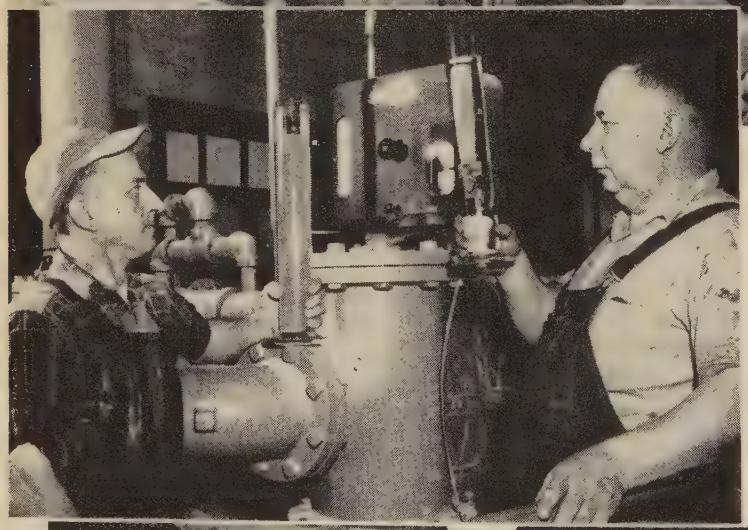


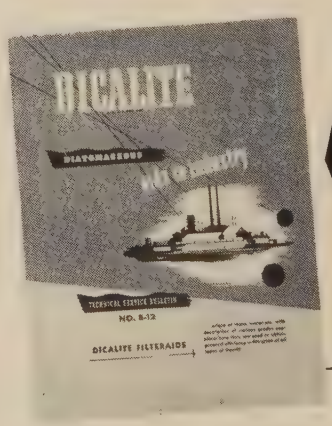
ABOVE—Three 1000-sq. ft. filters in use at Ohio Boxboard Co. mill for white water filtration. Bags of Dicalite Filteraid piled in background at right. Photo reproduced on NEXT PAGE shows the filter house, with existing settling and fresh water ponds (some to be eventually eliminated) in foreground and at left of the building.

LEFT—The two men are inspecting the water before and after filtration. Note the clarity of the filtered water on the right.

BELOW—Cleaning a filter at the end of a cycle. The filter cake, containing the Dicalite and the recovered fibers, goes to the hydropulpers for addition to the filler furnish.

LATEST DATA ON FILTRATION

Technical Bulletin B-12 covers the use of diatomaceous earth filteraids in filtration of all types of liquids, including operating and performance data on Dicalite materials. Copies on request without charge.



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on the job at OHIO BOXBOARD

...the industry's first large scale "Oco Water System" installation...The Ohio Boxboard Company uses Dicalite Filteraids with positive success in pressure filtration of white water

Seven and one-half years of pioneering research and engineering paid off last February when the Ohio Boxboard Company, Rittman, Ohio, put into operation the "Oco" white water clarification system using pressure filtration. Today after six months of successful operation, two of their four machines are running with improved efficiency on this system.

Almost from the start, Dicalite Filtration Engineers worked closely with the technical staffs of Ohio Boxboard Co., and Oco Water Systems, Inc., contributing from Dicalite's twenty years of industrial experience in the separation of solids from liquids. One of the regular grades of Dicalite filteraids is being used.

Ohio Boxboard has found that the installation benefits them substantially in many ways. It permits the recovery and re-use of fiber formerly wasted. It has reduced the water requirements on its #1 and #2 machines about 1000 GPM, and the filtered water has been found entirely suitable for continuous operation, with high pressure low volume showers, on felts and wires. The System in operation permits effective control of slime and odor-forming bacteria, and the use of the clear filtered water increases the brightness and cleanliness of the sheet of board made. They have noted an increase of from 10% to 15% in felt life, and the saving in power and steam usage, in itself, is reported to be sufficient to pay for the material and operating costs of the System. Obviously, as less water is required and used, less and cleaner water is discharged from the plant. Stream pollution, therefore, is decreased, and with the contemplated extension of this System to all of its machines, this objectionable industrial problem can be solved.

A filtration system which affords continuous re-use of practically all paper machine white water can be employed successfully in most board and paper mills. Such a system, using Dicalite filteraids, results in complete removal of suspended solids and at whatever volume output is necessary to meet the mill's water demands. The installation and operation of such a system is simple and requires a small space area. Cost of the equipment and its operation is relatively very low, while on the other hand investment returns are very high.

DICALITE DIVISION, GREAT LAKES CARBON CORPORATION

GLC

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More than half of the logs for pulpwood are cut in the field by gasoline or electric chain saws. The logs are from 30 to 60 feet long and up to 6 feet in diameter, averaging 1 to 2 feet. The logs are trucked to the nearest navigable water. Most of the wood for Camas is dumped into the Columbia River near its mouth. Some comes via the Williamette River. The logs are made into a flat raft containing about 200,000 board feet. Butt logs of hemlock are waterlogged on the stump. For floating to the mill, they are mixed with buoyant top hemlock logs and then gathered in round bundles tied with iron hoops. The flat and round rafts are floated to storage waters capable of holding several months' supply for the mill.

Two large jaw cranes lift the logs out of the river. The logs are cut to standard 24-foot lengths and carried by cross conveyer to a hydraulic barker (*13E*). Geared wheels rotate the logs up to 40 r.p.m. under a perpendicular jet of high-pressure water (1400 p.s.i., 1200 gallons per minute). One lengthwise pass of the jet is sufficient to erode off all the bark. The barker capacity is four to eight logs per minute, depending on diameter.

A more common and older method for removing bark is by means of a cylindrical drum made of iron angles. Logs (cut 2 to 4-foot lengths) enter continuously at one end and the rotation of the drum on the long axis tumbles them against each other and against the inside of the drum, wearing off the bark. After a retention time of 0.5 to 2 hours, the logs are continuously forced out the other end. Besides the bark, 5 to 6% useful wood, which represents waste, may be ground off. The hydraulic barker is displacing the drum counterpart in many mills.

From the hydraulic barker at Camas, the bark is sent to a waste heat furnace and the clean logs are conveyed to a chipper (*14E*). This is a 153-inch diameter heavy steel disk set with six knives and rotated at 257 r.p.m. by a direct-connected 1500-hp., 7000-volt synchronous motor. Logs up to 34 inches in diameter can be chipped. If the machine were supplied with a continuous stream of 30-inch diameter logs, it could convert to chips over 200,000 board feet of logs (400 cords) each hour. The Camas maximum daily requirement is about 650,000 feet board measure (1300 cords). After moving down a short chute, the logs press against the whirling chipper blades and are completely converted to chips. Screen analyses are taken daily and hand measurements weekly. Typical monthly average chip analyses by screening and hand measurement are shown in Table III.

Table III. Size of Wood Chips

Screen analysis		Hand measurement	
Screen size, in.	Retained, % of weight	Length, inches	% by weight
		Trash	0.5
		1 inch and over	3.0
1	1.8	7/8	9.5
3/4	18.4	3/4	34.2
1/2	46.4	5/8	38.0
1/4	30.2	1/2	10.5
1/8	2.2	3/8	2.7
		1/4	1.0
Through 1/8	1.0	Less than 1/4	0.6

The chips are screened (*1E*), and those over 1 inch long are sent back to a chip breaker; after this they are returned to the system. Anything under 0.25 inch long is considered dust and is sent to the steam plant. Those chips that are not going to be used immediately for pulp are conveyed to one of four storage silos. This permits segregation of four species of grades of wood.

The complex details of the kraft process can be better understood with the help of the following résumé: Wood chips are digested or cooked with an alkaline liquor. The active cooking chemicals (sodium hydroxide and sodium sulphide) dissolve the cementing lignin material of the wood. The liberated fibers (largely cellulose) and spent chemicals are separated on vacuum washers. At this point the fibers are ready for screening and subsequent papermaking.

The remainder of the process is concerned with recovery of the chemicals. Multiple-effect and disk evaporators remove water from the weak liquor until it is sufficiently concentrated to burn. In the recovery furnace, burning accomplishes separation of organic from inorganic chemicals by destroying the former; conversion of inorganic chemicals to sodium carbonate and sodium sulphide; and production of heat and power. All heat requirements of the kraft mill are supplied by the recovery furnace. The molten inorganic chemicals from the furnace are dissolved in water to form "green" liquor, which after clarification is treated with lime to regenerate sodium hydroxide. This liquor with its active constituents (NaOH and Na_2S) is "white" liquor which is then used for digestion of wood at the beginning of the pulping process. The lime spent in causticizing is washed, burned, and recycled.

STATIONARY DIGESTERS

The large cooking vessels known as digesters are generally stationary, but a few mills such as Camas use the tumbling or rotary type. Since the former is more commonly used in kraft pulping, it will be described first.

The stationary digesters of the Port Townsend, Wash· mill of Crown Zellerbach are typical of the industry. They are cylinders with a volume of 2500 cubic feet and are fitted with a bell top and cone bottom. They are built of $1^3/_{16}$-inch steel plate with over-all height of 35 feet and diameter of 10.5 feet. The rated capacity of each cook is 6.5 tons of pulp on an air-dry basis (10% moisture). Each digester is equipped with an external stainless steel two-pass tube heater (steam on outside) with a heating surface of 485 square feet.

Chips are run into the digester by gravity from overhead bins. The flow of chips is maintained by steam jets located near the bin bottoms; at the same time the cooking and diluting liquors are run into the top of the digester. The force of the streams packs the chips, thereby increasing the digester charge by about 10%.

The cooking liquor is circulated through the heater and digester by an 1800-gallon-per-minute centrifugal pump driven directly by a 50-hp. 870-r.p.m. motor. Liquor is pulled through a strainer one third of the way up the digester, forced through the heater, and returned to the digester in split flow—about one third to the bottom and two thirds to the top.

The active cooking chemicals are contained in the "white" liquor (see Fig. 5 for analysis) and amount to 15.5% on the dry weight of wood, with all chemicals

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expressed as Na_2O. A typical charge to a stationary digester comprises 760 cubic feet of white liquor, 525 cubic feet of black liquor, and 23 3 tons of wood chips (12.3 tons air-dry basis).

White Liquor Composition

	Lb. Na_2O/cu. ft.
Total alkali	6.68
Active alkali	5.78
Sulphide	1.52
Sulphate	0.23
Sulphite	0.11
Chloride	0.37

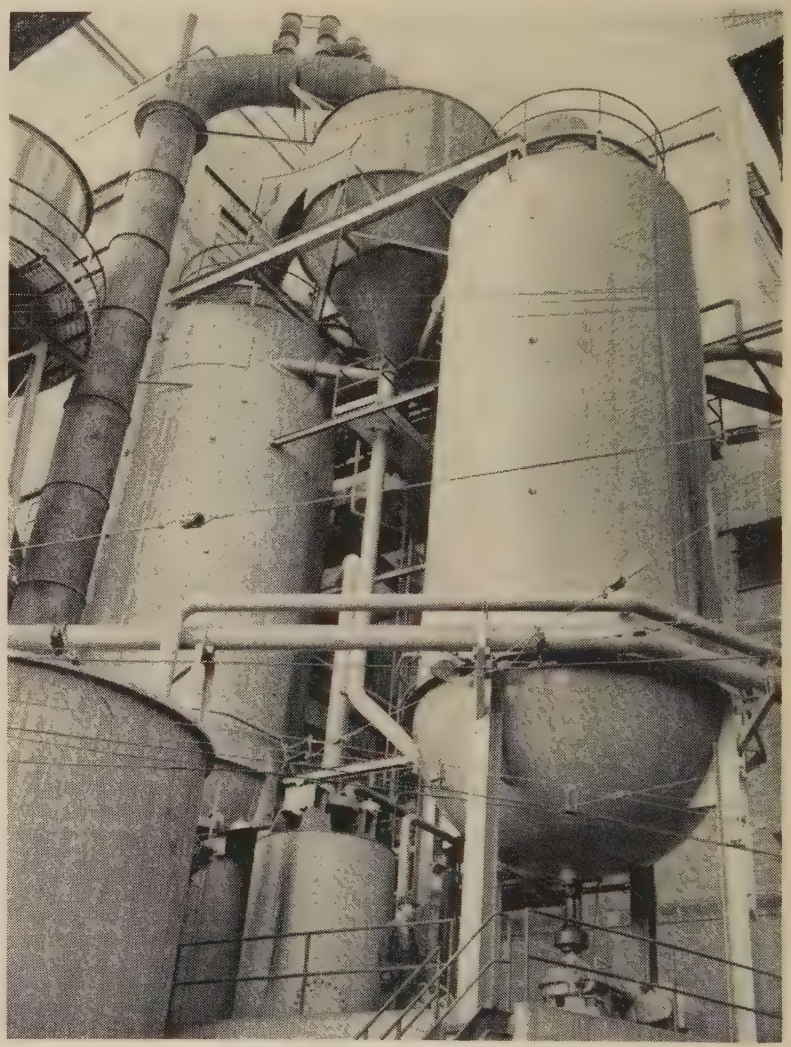
Sodium carbonate is inactive in the cooking process. A white liquor high in sodium sulphide is a very important factor in producing pulp of high strength and quality. A low sodium sulphide liquor resembles in cooking action that of the soda process which makes a low-strength pulp. The less drastic dissolving action of kraft cooking liquor accounts for its 10% greater pulp yield than in the soda process.

The role of sodium sulphide in kraft pulping is explained (*3*) as follows: lignin of wood reacts in the solid phase with sulphide ion. This appears to facilitate the subsequent cleavage of lignin from the fiber. The sulphur blocks active groups of the lignin, thereby preventing condensation to large insoluble molecules. The cooking liquor then dissolves the lignin which has been rendered more soluble by its reaction with sulphur.

In the stationary digester enough black liquor (Fig. 5) (comprising 40 to 45% of total liquor volume) along with white is added to cover the chips. Black liquor is used instead of water for volume make-up in order to eliminate dilution of liquor which would increase the load on the evaporators and subsequent recovery.

The cook is brought to 344°F. and 110 p.s.i. as rapidly as possible; this requires 2 hours. Temperature is maintained for about 25 minutes with adjustment of the exact time by examination of pulp samples blown from the digester. Pressure is relieved to 80 pounds and the digester blown to a blow tank through a cyclone separator.

In a kraft cook it is important that air in the digester and in the pores of the chips be relieved as early as possible because oxygen has a powerful degrading action on cellulosic materials in the presence of hot alkali. Air removal is accomplished by venting the top of the digester to the atmosphere. The end point of the relief is reached when the steam pressure and temperature correspond.



Digester blow tanks, cyclone separator, and pipe line to steam heat recovery

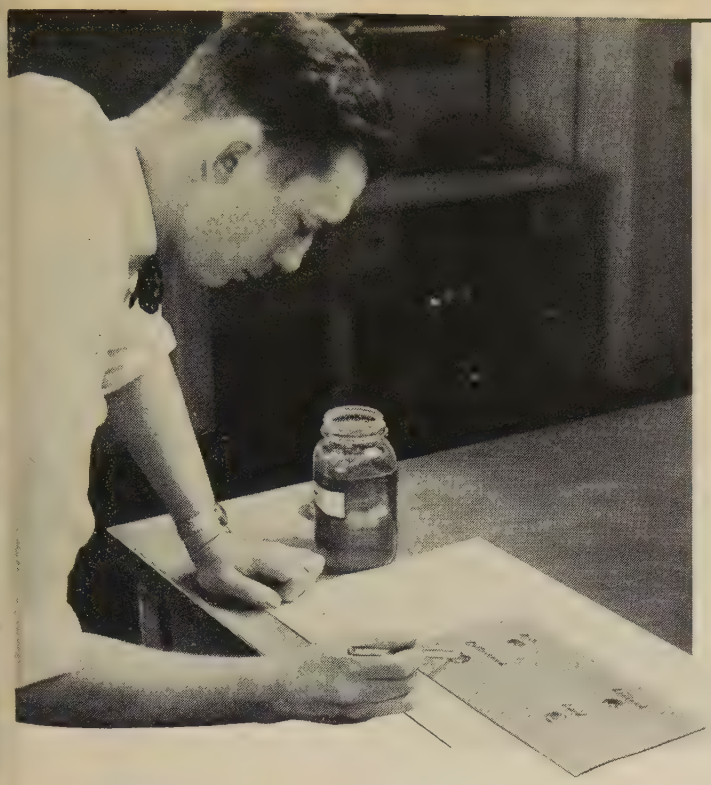
ROTARY DIGESTERS

Wood digestion is accomplished at Camas in ten rotary or tumbling digesters (*5E*). Each of five units is 9 feet 10 inches in diameter, 26 feet high, has a volume of 1460 cubic feet, and can cook 3.5 tons of pulp (air-dry basis). Each of the remaining five units is 10 feet 3 inches in diameter, 30 feet high, with a volume of 1884 cubic feet, and can cook 4.5 tons of pulp (air-dry basis).

The digester is mounted on trunnions attached to a heavy reinforced central section. This arrangement has been found superior to mounting on a shaft through the shell. Previous digester shells expanded more than the shaft allowed, causing accelerated corrosion in the stressed area.

The digesters are built with a safety factor of 5, based on the tensile strength of the steel. Use of an all-stainless steel shell would be prohibitively expensive; therefore, the necessary structural strength is obtained with 1.25 inches of steel boiler plate. Six units are lined with Type 405 stainless steel, $^7/_{64}$ inch thick, and resistance welded. Stainless steel linings being tried by other pulp manufacturers include Types 304, 316, and 347. The four unlined digesters are made of high silicon steel because it is cheaper and more corrosion resistant than ordinary boiler plate.

Alloy linings are used for several reasons. They have longer life against the gradual corrosion of the alkaline liquor. More frequent replacement of ordinary steel digesters is expensive from a material as well as labor standpoint. The life of an unlined digester made of boilerplate is estimated at 10 years based on a



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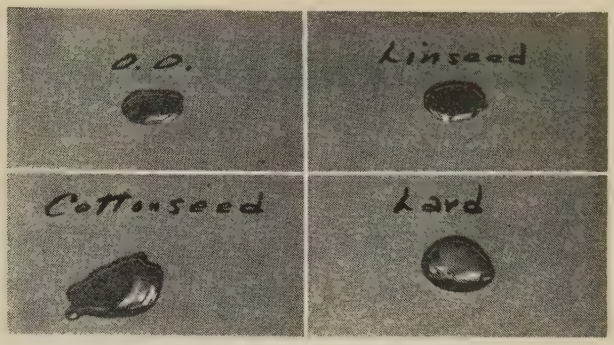

GREASE TEST—HOURS FOR PENETRATION

	Kraft	Chipboard
Olive Oil	120 +	120 +
Lard	120 +	120 +
Cotton Seed Oil	120 +	120 +
Linseed Oil	120 +	120 +

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penetration of 1/16 inch per year. An all-high silicon steel unit can be used for 12 years.

In recent years, alloy steels have become cheaper and the methods of fabrication have improved greatly. Welding can be done in the field instead of in the shop. Stainless steel is available as either resistance-welded or rolled onto the steel shell. This applies not only to the digester but wherever alloys are justified. All of the digesters are insulated with 1.25 inches of magnesia blocks cemented with a waterproof mastic emulsion protective covering.

A digester is charged by rotating it to the vertical position, then filling with wood chips from an overhead bin (Fig. 2). The cooking liquor is run in at the same time from a calibrated tank. Charge to the five smaller units comprises 23,500 pounds of cooking liquor and 26,000 pounds of wood (50% moisture). Charge to the five larger units comprises 30,000 pounds of cooking liquor and 33,500 pounds of wood (50% moisture).

The digester is rotated at 0.2 r.p.m., and the wood is cooked with direct steam at a pressure of 110 p.s.i. (340°F.). The steam input is automatically cam-controlled by means of a time-pressure template (*10E*). Heat-up requires 1.25 hours; then the charge is held at 340°F. for an additional 0.75 hour, after which the pressure is relieved to 80 p.s.i., then sampled and blown. The sample is usually taken one or two rotations before the pulp is expected to be completely cooked to permit any necessary changes in cooking time.

The pulp is blown tangentially into the top of the blow tank. Steam is exhausted from the top to a heat exchanger (1760 tubes, 16 feet long, 1 inch outside diameter). The heat given up to process water outside the tubes is the sensible heat from 340° down to 212°F. plus the latent heat of condensation (*17E*). Meanwhile, the pulp and black liquor (Fig. 5) drop to the bottom of the blow tank. For each ton of pulp, the associated black liquor contains 3000 pounds of solids, of which 1300 pounds are recoverable chemicals. The remainder comprise the organic solids from the wood.

The blow tank is 40 feet high, 14 feet in diameter, and made of 3/8-inch mild steel plates. An agitator on a vertical shaft extends through the bottom to mix the stock with additional black liquor. This is spent liquor formed in previous digestions and separated from the pulp at the washers. Dilution is necessary to obtain sufficiently low consistency for pumping. The stock in the blow tank and consistency regulator is diluted from 15 to 2.5% solids.

The consistency regulator is a steel tank 8 feet high and 4 feet in diameter fitted with blades pitched slightly upward. A central shaft, turned by a 2-hp. motor, is also fitted with blades. As the pulp consistency increases, the load on the motor increases, as measured by a potentiometer, and an air-actuated device opens vents to admit more black liquor to dilute the stock. When this happens, the load on the motor which drives the paddles is decreased to a point where the black liquor flow will be throttled. Consistency must be controlled within narrow limits in order to form a uniform mat of optimum thickness on the following washers.

A 40-hp. variable-speed motor drives a centrifugal pump running 800 to 900 r.p.m. (maximum speed 1200 r.p.m.) which sends the pulp to knotters (*3E*) for removal of knots and oversized chips. Knotters are a series of flat vibrating screens with 3/8-inch round openings. Stainless-steel screens are now used after it was found that for some unknown reason mild steel screens clogged more readily, causing poor separation of sizes.

Vapor heads of sextuple-effect evaporators showing arrangement in limited space

The rejects are conveyed back to be mixed with chips entering the digesters, where a second cook will defiber the knots and oversize chips. Pulp which passes through the holes goes by gravity to the washers.

It is necessary to wash the maximum amount of chemical from the pulp with a minimum amount of water, hence multiple-stage washing. This is accomplished in two 2-stage rotary vacuum washers in series so that in effect the washing is 4-stage (*16E*). The effluent is pumped and showered on the pulp mat countercurrent to the pulp flow. Between the first and second washer or between the second and third stages there is an interpulper which is a small tank with agitator. Effluent from the third stage dilutes the pulp to 1% or less consistency; it then goes to the second washer or the third stage of the system to form a mat. The pulp coming off the washers is 17% consistency. Hot water at 150°F. is added to the mat only on the last stage. The capacity of the washers is about 1.2 tons of pulp per square foot of wire surface per 24 hours. Vacuum on the wire is 8 to 10 inches of mercury. The pulp at this point leaves the pulp mill for the screen room where it is screened and further treated for bleaching and the paper machine (Fig. 2).

EVAPORATION

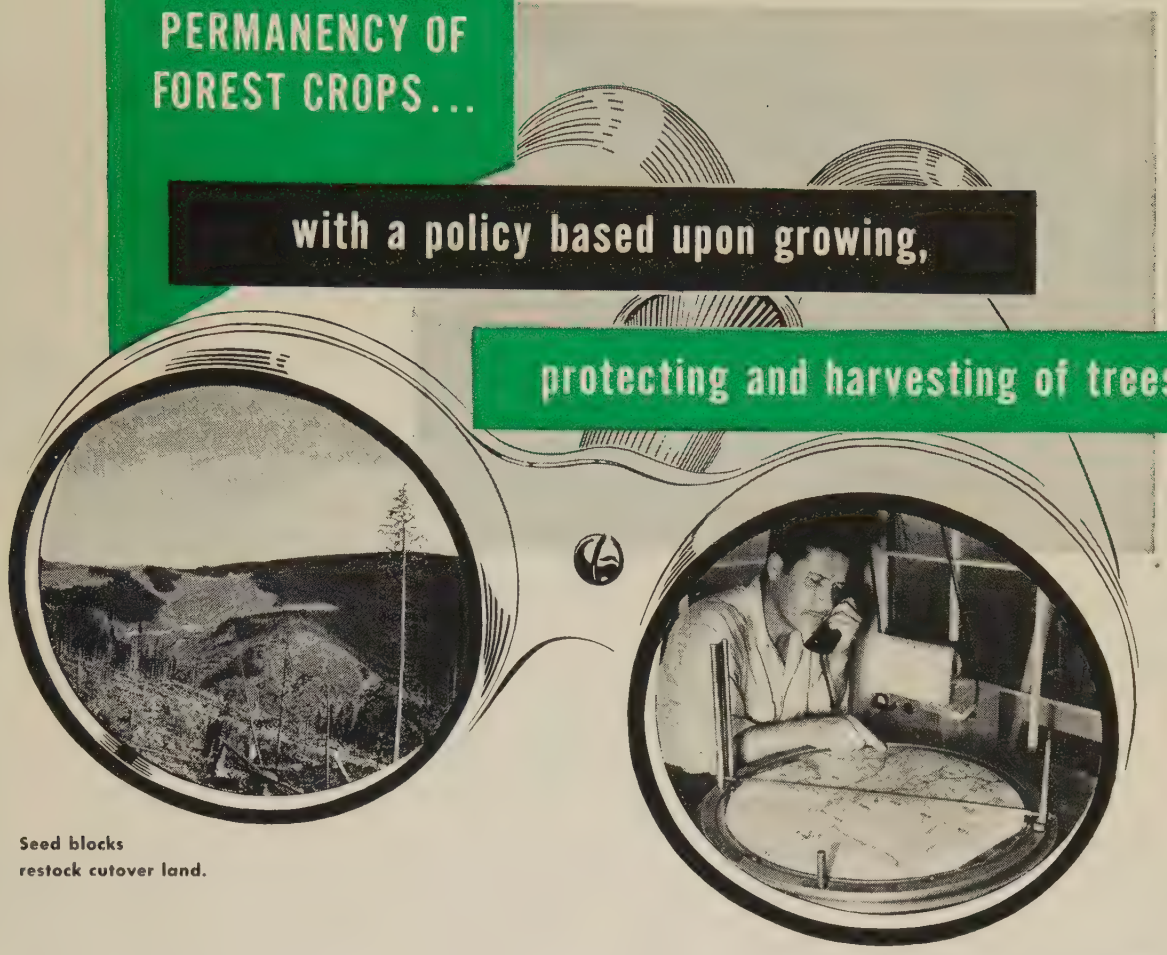
The function of the evaporators is to remove water, or concentrate the weak black liquor (Fig. 3) from the washers to such a density that when it is sprayed into the recovery furnace it will ignite and burn because of the organic matter content. At Camas this concentration is done in two types of evaporators: multiple effect steam evaporators and direct heat or disk evaporators using hot gases from the furnace (Fig. 3).

Sextuple-effect vertical-tube rising film evaporators (*15E*) have been found most effective for concentrating the liquid from about 15 to 18% to 48 to 54% solids. One pound of steam evaporates 4.7 pounds of water in this evaporator but sometimes greater economy is ob-

LOOKING TOWARD PERMANENCY OF FOREST CROPS...

with a policy based upon growing,

protecting and harvesting of trees.



Seed blocks restock cutover land.

Spotter plotting a fire location.

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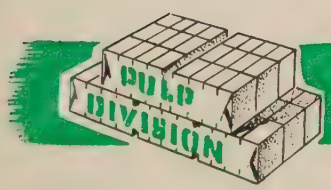

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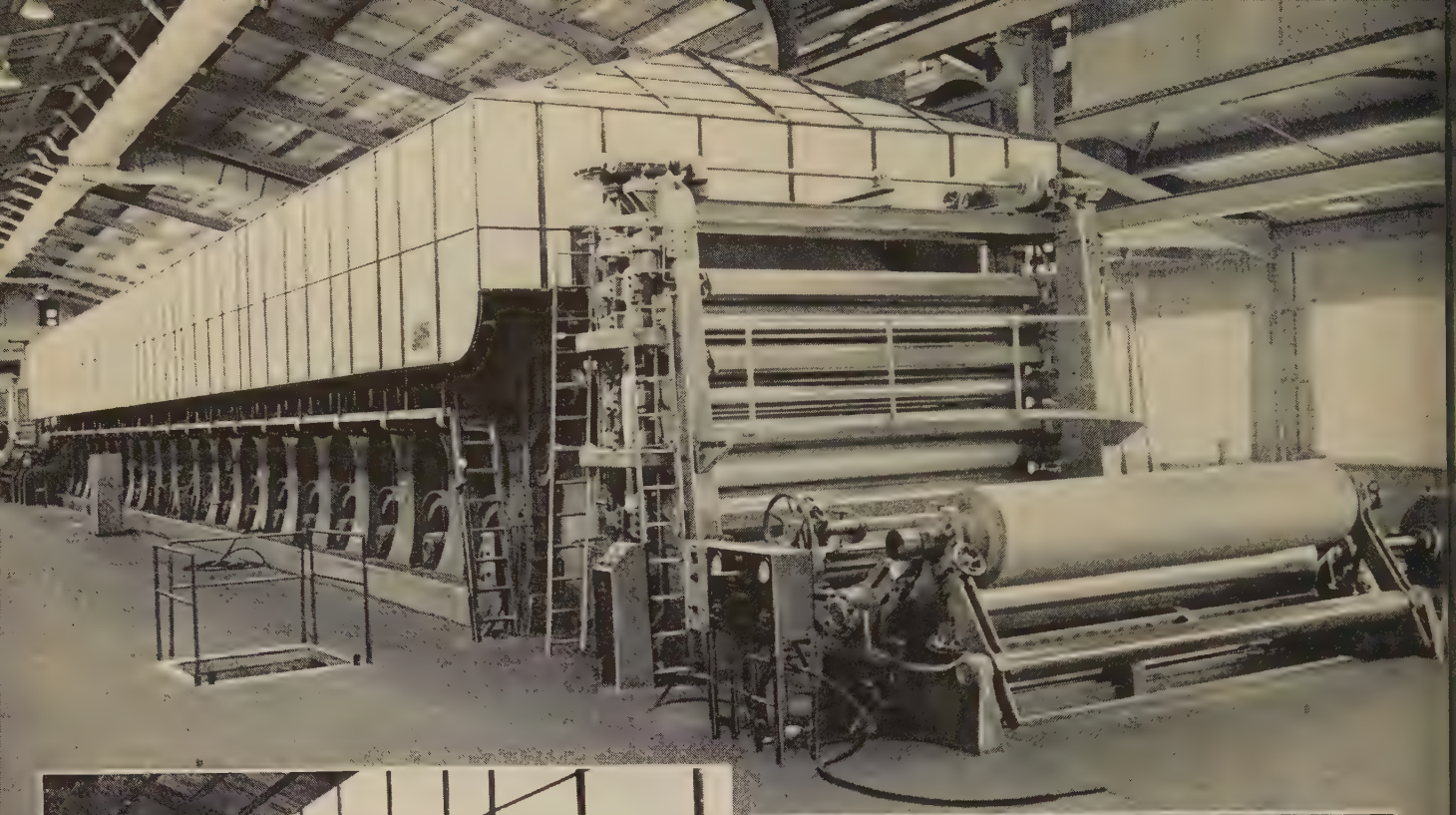

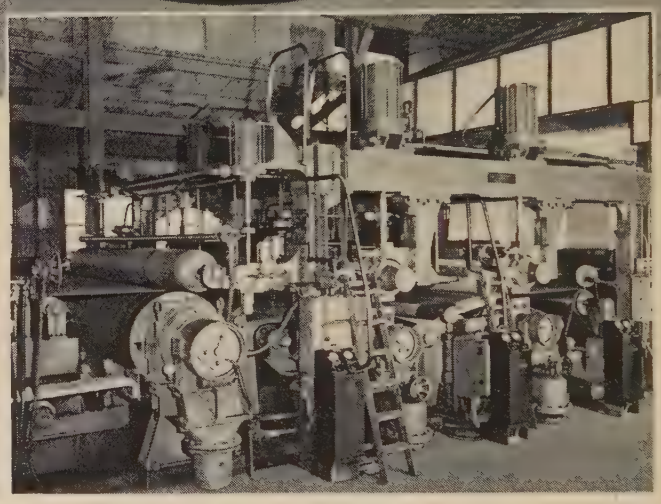

FEATURES OF 160" PUSEYJONES FOURDRINIER MACHINE AT CALCASIEU

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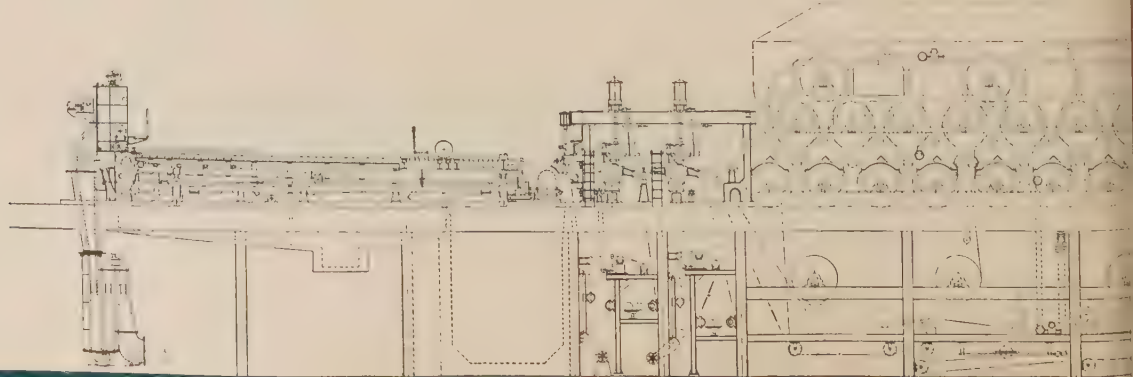
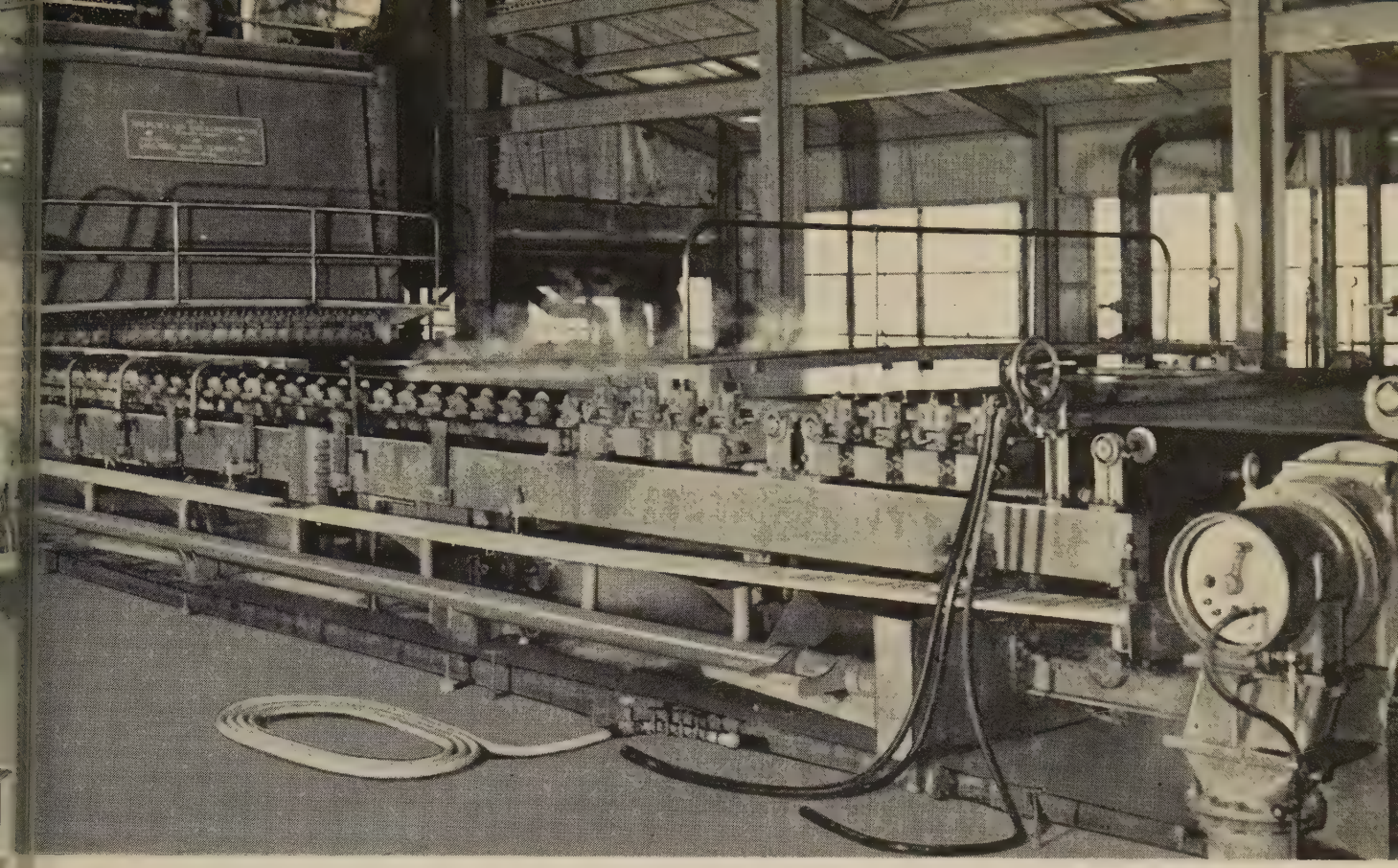
Pope type Uniform Speed Reel of improved design, with pneumatic adjustable loading mechanism.

Unwinding stands with water-cooled friction brake.

Puseyjones Winder with hydraulic-operated roll unloading mechanism.



Line drawing of new machine. Designed and constructed for maximum operating speed of 1500 feet per minute of Kraft bag and wrapping papers with G.E. sectional motor drive.



MORE PRODUCTION FOR CALCASIEU

Shown here is the new 160-inch Puseyjones Fourdrinier Machine in operation in the new, modern plant addition of the Calcasieu Paper Company Plant, Elizabeth, La., the latest unit installed in the South for the production of Kraft bag and wrapping paper. The latest features in machine design from Wet End to Winder have been incorporated in this new machine for more efficient, higher tonnage Kraft production.

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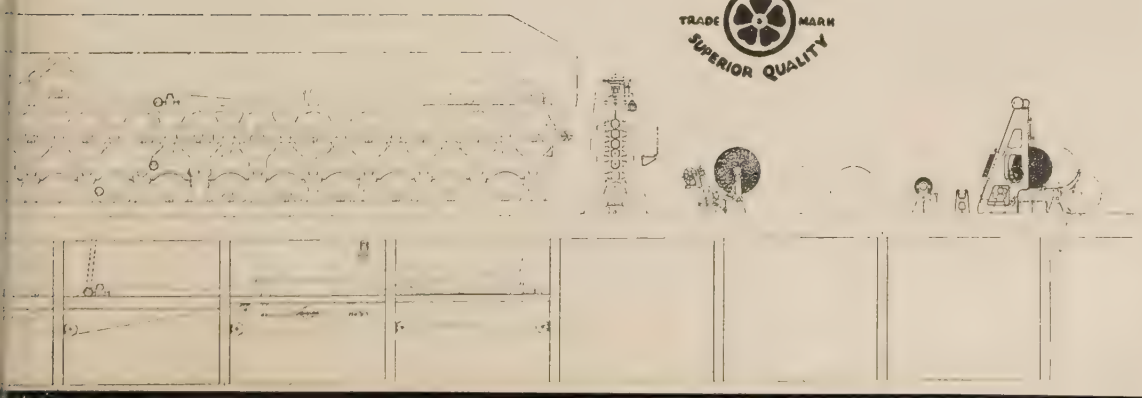

All rolls and rotating parts in the new Puseyjones Fourdrinier Machine at Calcasieu, with the exception of the lower calender roll, are equipped throughout with anti-friction bearings.

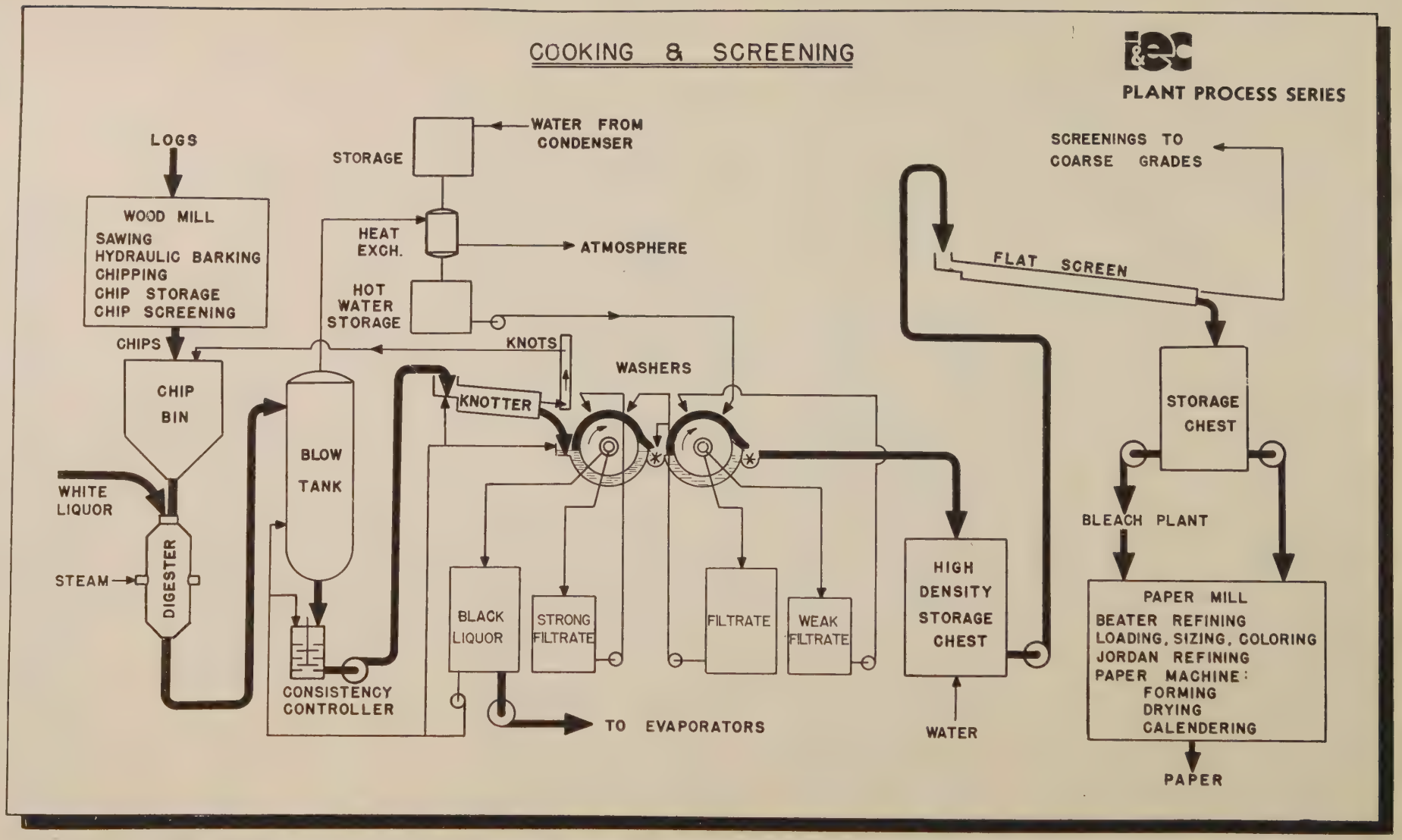

Fig. 2. Flow sheet of cooking and screening processes in production of kraft pulp at Camas, Wash., mill of Crown Zellerbach Corp.

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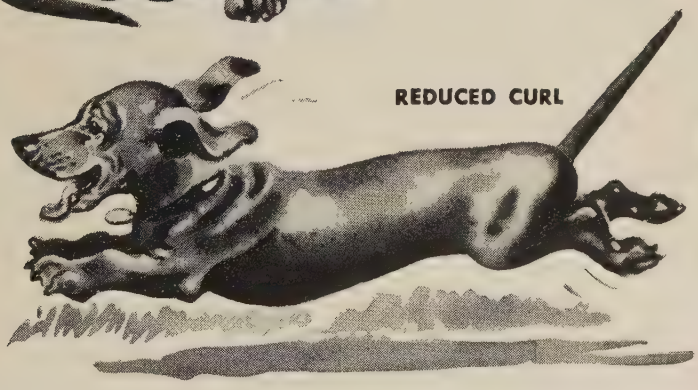

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tained (Table IV). It is common practice to use stainless steel—for example, Type 430—in the first effect because of the corrosive nature of the alkaline liquor at elevated temperatures. The vapor head also has an alloy protection (coating welded to the steel shell). Each evaporator contains 552 2-inch outside diameter tubes, 24 feet long. After the first effect, the tubes in all other effects are ordinary steel. The diameter of each steam chest is 4 feet and dome diameter is 8 feet. The evaporator has an over-all height of 35 feet and the shell is 0.5-inch steel plate. The surface condenser for the evaporator system contains 1146 tubes, 13 feet long and 1 inch outside diameter. Vacuum is obtained by twin-steam ejectors sometimes used in series. In the operation of the sextuple effect evaporators the weak liquor is fed directly into effects V and VI in equal

Table IV. Sextuple-Effect Evaporator Test

Material Balance

	Lb./hr.
Feed of weak black liquor = 2850 cu. ft./hr. × 1.09 (sp. gr.) × 62.4 lb./cu. ft.	194,000
Discharge from evaporator = 194,000 lb./hr. × $\frac{17.5\ (\%\ \text{solids in inlet liquor})}{53.3\ (\%\ \text{solids in discharge liquor})}$	63,700
Total evaporation of water accomplished in evaporator	130,300

Lb. H_2O evaporated/lb. steam = $\frac{130{,}300\ \text{lb./hr. (total evaporation)}}{26{,}000\ \text{lb./hr. (steam consumption)}} = 5.01$

	Flash tank	*Evaporator test effect*[a]					
		I	*II*	*III*	*IV*	*V*	*VI*
Chest pressure, lb./sq. in. gage	...	36.5	15.0	9.2	−4.0[b]	−15.0[b]	−21.2[b]
Chest temp., °F.	...	282	249	226	205	179	156
Temp. difference, °F.		21	12	12	14	11	31
Liquor temp. calcd., °F.	217	261	237	214	191	168	125
Liquor temp. measd., °F.	206	263	234	210	186	164	129
Boiling point rise	11	11	10	8	7	5	6
Dome temp., °F.	206	250	227	206	181	163	119
Dome pressure, inches Hg	...	30.8	10.5	−3.5	−13.3	−19.6	−26.7
Latent heat of vaporization B.t.u./lb./°F.	974	946	961	974	990	1000	1026
Total solids, lb., %	53.3		37.9	31.3	25.9	22.4	24.3
Total solids, calcd., %	...	51.4					
Feed, lb./hr.	66,000	90,000	108,500	131,000	145,300	95,300	98,700
Discharge, lb./hr.	63,700	66,000	90,000	108,000	131,000	74,300	71,000
Evaporation, lb./hr.	2,300	24,000	18,500	23,500	14,300	21,000	27,700
Evaporation (heat bal.), lb./hr.	2,240	23,500	21,700	22,100	19,800	22,300	28,500
Over-all temp. difference, %	...	20.8	11.9	11.9	13.8	10.9	30.7
Acceptance test No. 1	..	30.8	7.5	9.4	15.0	15.0	22.4

Heat Balance

	Q (heat requirement), M B.t.u./hr.	*Latent heat of vaporization, B.t.u./lb./°F.*	*Lb. H_2O evaporated*	*Effect*
Liquor flash[c] (66,000) (261 − 217) (0.75)	2,180	974	2,240	Flash tank
Steam feed (26,000) (923)	24,000			
Heat liquor to I (90,000) (261 − 237) (0.83)	−1,790			
B.t.u. to II from evaporation of liquor	22,210	946	23,500	I
Steam condensate flash (26,000) (282 − 249)	860	946	910	
Total B.t.u. to II	23,070		24,410	
Heat liquor to II (108,500) (237 − 214) (0.87)	−2,170			
B.t.u. to III from evaporation of liquor	20,900	961	21,700	II
Steam condensate flash (26,000 − 910) (249 − 226)	580	961	600	
Condensate flash (24,410) (249 − 226)	560			
Liquor flash	2,180	974	2,240	
Total B.t.u. to III	24,220		24,540	
Heat liquor to III (131,000) (214 − 191) (0.89)	−2,680			
B.t.u. to IV from evaporation of liquor	21,540	974	22,100	III
Condensate flash (24,410 + 24,540) (226 − 205)	1,030			
Total B.t.u. to IV	22,570			
Heat liquor to IV (145,300) (191 − 168) (0.90)	−3,010			
B.t.u. to V from evaporation of liquor	19,560	990	19,800	IV
Condensate flash (24,410 + 24,540 + 22,100) (205 − 179)	1,850			
Total B.t.u. to V	21,410			
Cool liquor to V (95,300) (168 − 178) (0.92)	880			
B.t.u. to VI from evaporation of liquor	22,290	1000	22,300	V
Condensate flash (24.410 + 24,540 + 22,100 + 19,800) (179 − 156)	2,090			
Total B.t.u. to VI	24,380			
Cool liquor to VI (98,700) (125 − 178) (0.92)	4,810			
B.t.u. to condenser from evaporation of liquor	29,190	1026	28,500	VI
Total for the 6 effects	139,650,000		140,100	

Six-unit over-all head coefficient: $U = \frac{Q}{A\ \Delta t}$ A = 4433 sq. ft. av. $U = \frac{139{,}650{,}000}{4433 \times 101} = 315$

[a] Total temperature difference in 6 effects = 101°F.; inlet weak black liquor temperature = 178°F.; barometric pressure on 9/29/49 = 30.05 inches Hg.
[b] Inches of mercury.
[c] (Lb./hr. feed) (temp. diff.) (spec. heat, B.t.u./lb.).

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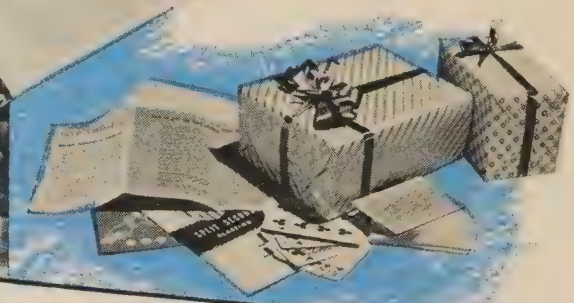

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parts. The vapor flash from effect I enters the dome of effect IV.

Because this is one of the few places in industry where sextuple-effect evaporation is regularly carried out, Table IV has been prepared to show material and heat balances taken on Sept. 29, 1949. In comparison with the first acceptance test made by the manufacturer, this test showed a higher evaporation per pound of steam and a slightly lower over-all sum of temperature differences between vapor side and liquor side. This indicated that the tube surfaces, inside and out, were in good condition and that this type of evaporator was well designed for its required service.

eter and contains a shaft 8 feet long with 33 disks set on $2^5/_8$-inch centers. A motor drives the shaft at 4 r.p.m. causing the disks to rotate in the pool of liquor at the bottom. The liquor sticks to the disks and the hot furnace gases pass over them evaporating some of the water: inlet liquor concentration, 48 to 54% total solids; outlet, 58 to 62%; inlet gas temperature, 380°-F.; outlet, 325°F. After leaving the disk evaporator, the liquor is pumped to storage where it is maintained at 190 to 212°F. by circulating through a tubular heat exchanger countercurrent to steam.

From storage, the strong black liquor is pumped to a mixing tank where dust collected from the Cottrell pre-

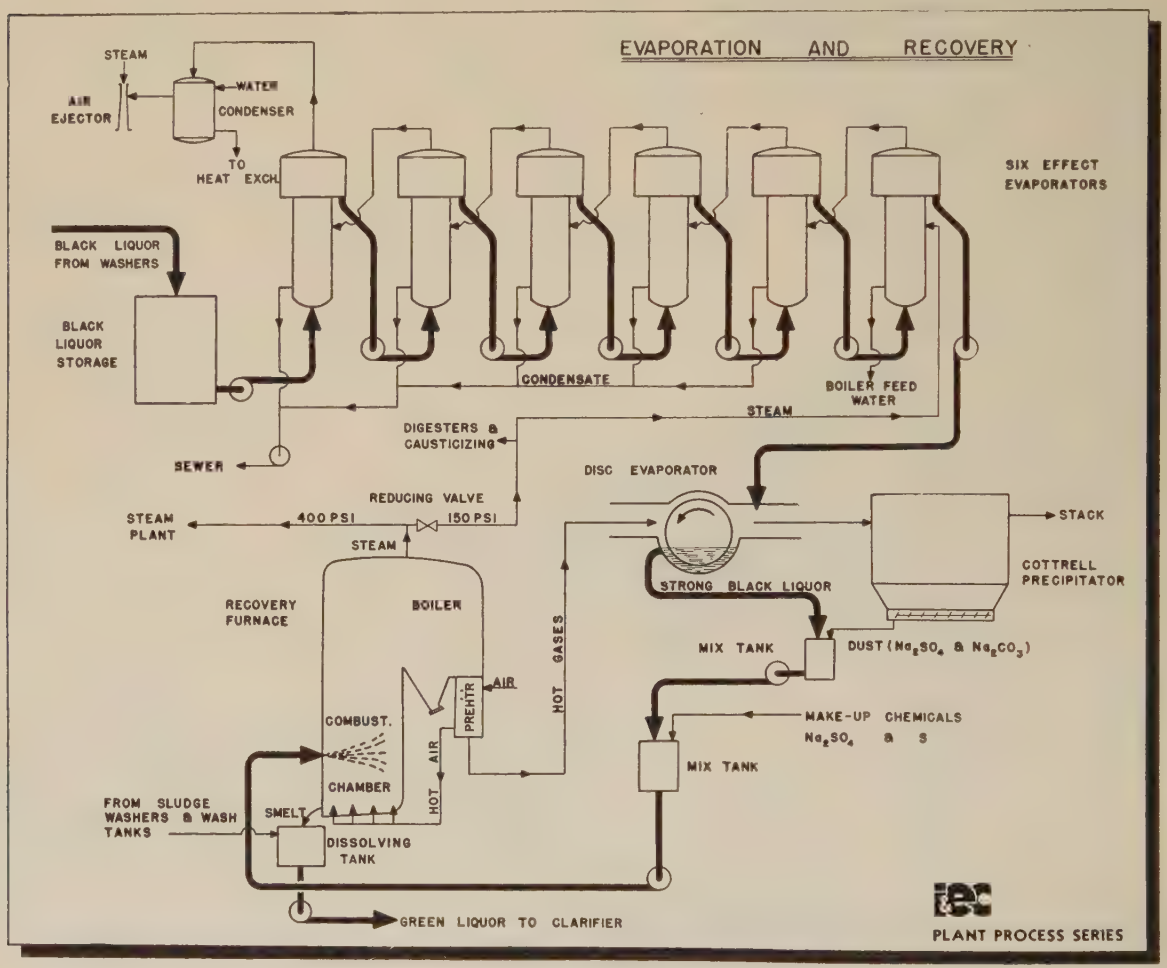


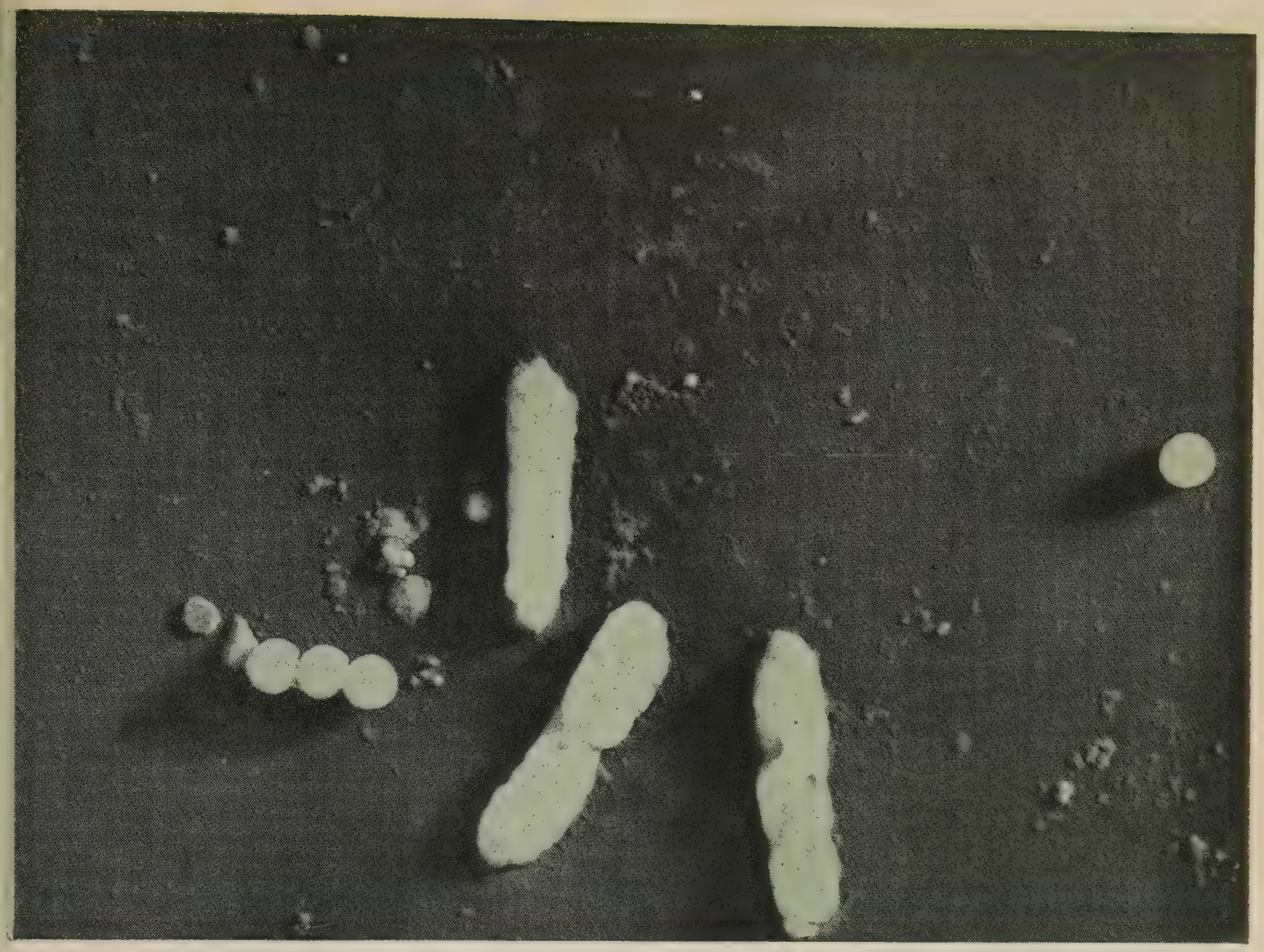
Fig. 3. Evaporation and recovery of chemicals in production of kraft pulp

Evaporation is carried out in the sextuple-effect evaporator until just before the liquor becomes too viscous to move freely through the tubes without forced circulation. Further concentration is done in two disk evaporators. This type takes advantage of heat that otherwise would be wasted out the stack. The heating gas used to concentrate the liquor comes directly from the waste heat boiler of the spray-type recovery furnace after heat has been removed by an economizer (to heat boiler feed water) and an air preheater (for forced draft).

Each of the two disk evaporators is 8.5 feet in diam-

cipitators is added. Then the liquor is pumped to another mixing tank where salt cake (Na_2SO_4) and sulphur are added continuously by means of an automatic weighing device that can be set to a predetermined feed rate depending on the amount of liquor being burned. The salt cake is the make-up chemical for all the soda losses in the process. Sulphur is used to control the sodium sulphide content of the cooking liquor.

The liquor from the second mixing tank is pumped through a heater in which steam is injected directly to increase the liquor temperature to 220°F. It is then sprayed into the recovery furnace.



An example of Salmonella Typhosa Bacteria, magnified 30,000X by Electron Microscope.

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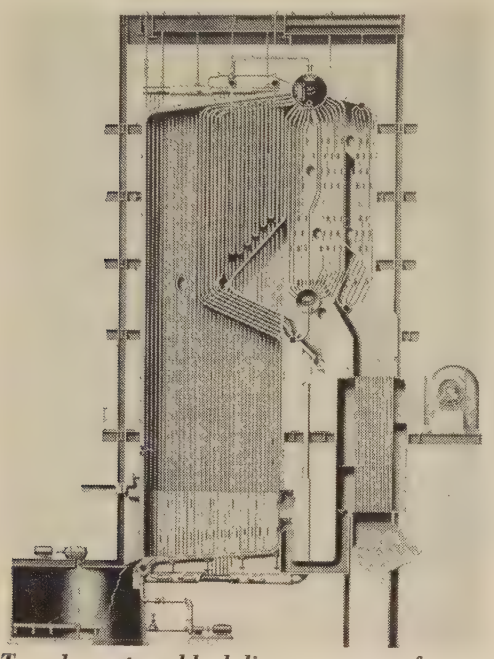
RECOVERY FURNACE

The spray-type recovery furnace (*4E*) has displaced the old type rotary furnaces (*5*). It is rectangular in design and the walls are built entirely of water tubes with plastic chrome refractory cement between them. The water walls on all four sides of the furnace are connected into mud drums at the bottom and into headers at the top which are so connected to the boiler drums that boiler water is circulated continuously through the walls. The furnace becomes a part of the waste-heat boiler. The side-water walls are carried under the hearth to the central mud drum and cool the refractory used to build up the sloping hearth of the furnace.



Two-drum-type black liquor recovery furnace

The boiler is a two-drum two-pass unit capable of generating 12,000 pounds of steam per ton of pulp at 400-p.s.i. pressure. The increased steam recovery is one of the chief advantages of this furnace. It was designed to burn 600,000 pounds of solids per 24 hours and produce 104,000 pounds of steam per hour. Before the furnace was installed, the kraft mill "bought" large quantities of steam from the central steam plant. This is no longer necessary. The recovery furnace supplies enough steam for cooking, evaporating the black liquor, and other smaller plant uses (Table V).

Table V. Steam Requirements

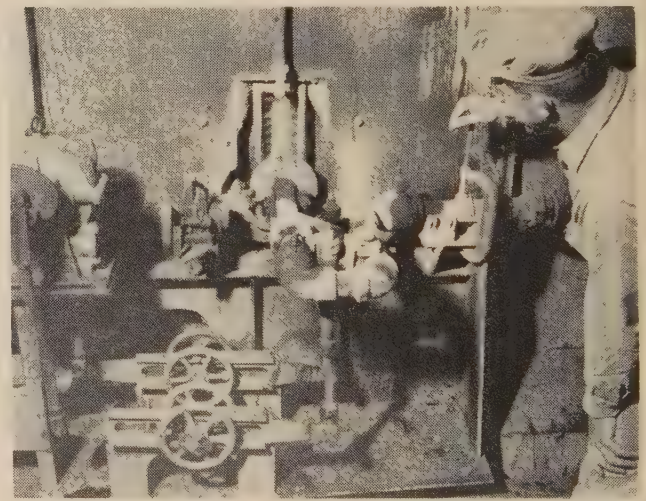
Use	*Quantity of steam used,[a] lb./ton air-dry pulp*
Black liquor evaporation	3,400
Pulp digestion	3,100
Causticization	400
Furnace operation, feed water heating, plant heating, etc.	200
Excess steam to central steam plant	3,900
Steam generated in waste heat boiler of recovery furnace	11,000

[a] The equivalent of 1600 lb. per ton are recovered as hot water from the digester blow gases; this water is subsequently used for pulp washing, etc.

Air enters the furnace in the side and back walls through primary air nozzles located 2.5 feet above the hearth and through secondary nozzles 15 feet above the hearth. A centrifugal blower moves the air that passes through a heater before entering the furnace. This heater raises the air temperature to 380°F. Air flow to the furnace is controlled by raising or lowering dampers in the nozzles and also by varying the pressure at the blower. Excess air is avoided because it will oxidize carbon directly to carbon dioxide, thereby destroying its ability to reduce salt cake to sodium sulphide. Incomplete salt cake reduction lowers the amount of sulphide in the cooking liquor and increases the inert sulphate load.

For best operation, the air input is kept to not more than 105% of theoretical. Above this there would be increased carry-over (largely sulphate) which builds up boiler-tube-bank accumulations difficult to remove. There would also be irregular burning to the point of ignition loss. As the excess air is reduced, the concentration of sodium carbonate in the carry-over will be higher; there will be incomplete combustion and reduced steam production. Successful operation of the spray-type furnace requires careful adjustment of air input within a narrow and critical range.

The liquor is sprayed into the furnace at 35 p.s.i. pressure through a hardened steel nozzle $^{7}/_{8}$ inch in diameter. The liquor strikes a flat stellited surface deflector plate or distributor plate set at 50° with respect to the line of liquor flow. The spray nozzle is given a two-directional oscillating motion so that the spray reaches all parts of the furnace walls. The size, angle, and oscillating motion are all critical to the efficient performance of the furnace in order to give the proper distribution of the liquor through the furnace for maximum evaporation of water prior to burning.



Device for oscillating nozzle of Tomlinson recovery furnace

The spray nozzle is 10 feet above the hearth. The combustion chamber is 64 feet high, 15.5 feet wide, and 17.5 feet long. The liquor in passing through the chamber is partially concentrated so that it is in the form of large uniform sticky drops when it reaches the furnace walls. These drops adhere and are further dried out. This gradually builds perhaps a foot of char which then falls onto the hearth where it is burned by the primary air. Black liquor has a heating value of

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about 6500 B.t.u. per pound on a dry basis. The organic portion of this has a heating value of 11,000 B.t.u. per pound on dry basis. If the liquor were atomized instead of distributed as large drops, the organic matter would be oxidized directly to carbon dioxide by the secondary air. This would eliminate the reducing zone near the primary air inlet, thereby preventing formation of sodium sulphide, defeating one of the furnace purposes.

COTTRELL PRECIPITATORS

The hot gases (14.5% carbon dioxide, 0.1% carbon monoxide, and inorganic chemical dust) generated from burning the black liquor pass up through the furnace and boiler, leave an air heater at 410°F., go through an induced draft fan, are cooled to 325°F. in the disk

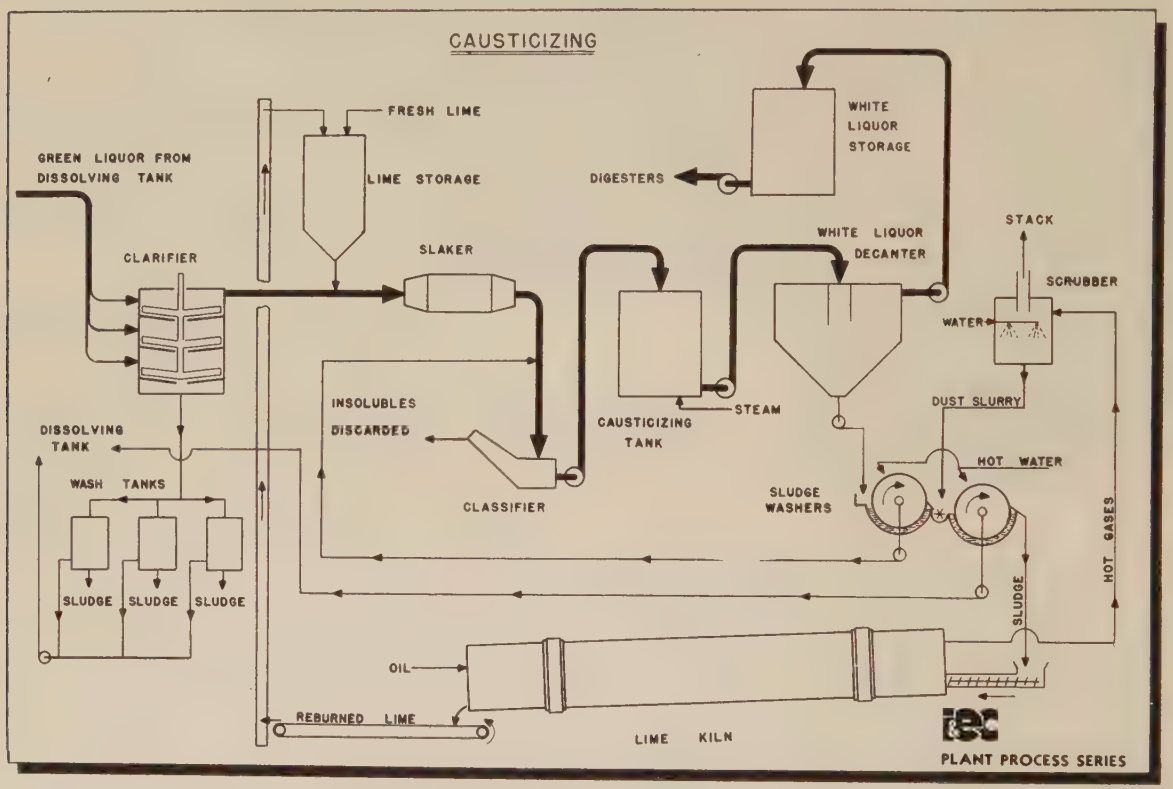

Fig. 4. Causticizing operation in production of kraft pulp

evaporator, and enter at 320°F. four Cottrell electrostatic precipitators in parallel (*18E*). Two are 12 by 12 feet with a rated combined capacity of 65,000 cubic feet of gas per minute. Two are 12 by 18 feet with a rated capacity of 100,000 cubic feet of gas per minute. This is based on 95% precipitating efficiency. The larger units were necessary to take the increased load of a new recovery furnace built after the original two precipitators were installed.

Each unit is divided into three sections in series. The units are paired so that four mechanical rectifiers are used to step up the 440-volt inlet current to between 45,000 and 65,000 volts for the six sections of two units. One rectifier supplies the two inlet sections; another supplies the two inner sections. However, the two exit sections are supplied by two rectifiers. This makes possible a higher potential and thereby precipitates more completely the less concentrated suspended solids in the exit sections.

Particles in the gas carry a slight negative charge. While passing through the Cottrell this charge is increased until the particles are attracted to the positive or grounded pole. They are held there by physical forces until removed by a mechanical rapping device which knocks them into a hopper for removal by a screw conveyer. The dust, largely sodium sulphate and sodium carbonate (Fig. 5), is returned to the recovery furnace to be reprocessed. For every ton of pulp produced, the Cottrells precipitate 100 to 120 pounds of dust.

The dust-free gases pass to a booster fan (capacity 133,000 cubic feet per minute) and then to a stack (150 feet high and 12-foot top diameter). An air-controlled damper after the booster fan maintains the Cottrell chambers at 0.2 inch of water vacuum.

While the char burns on the furnace hearth, the caustic soda, which was combined with the organic matter in the black liquor, is converted mainly to sodium carbonate. The salt cake and Cottrell dust that were added to the black liquor before burning are converted to sodium sulphide. Enough salt cake must be continually added to make up for soda and sulphide lost in the cycle. It is the presence of sodium sulphide in the kraft cooking liquor that differentiates this process from the soda process. Many chemical reactions occur at this stage of the recovery process, but the two principal ones can be represented as follows:

$$2NaR \text{ burns to} \rightarrow Na_2CO_3 + CO_2 + \text{Heat}$$

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where R represents the organic matter of black liquor.

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$

where C represents the carbon of black ash.

As burning of the ash and these reactions proceed, the smelt (melted Na_2S and Na_2CO_3) runs out the front of the hearth through water-cooled spouts and into a dissolving tank of water, there forming "green" liquor. This is so named because of its green color which is due to the presence of ferrous sulphide, a trace of ferric sulphide, and some finely divided ash from the furnace.

CAUSTICIZING

The green liquor (Fig. 5) is pumped to a three-tray clarifier, 9500 cubic feet capacity, 32 feet in diameter (*7E*), where the unburned carbon (0.3% on basis of liquor and lime slurry are added at the bottom of one causticizing tank, overflow to the second one, and the resulting mixture of sludge and white liquor is pumped continuously from it to the white liquor decanters. The causticizing tanks are heated with direct steam, maintaining a temperature of 215 to 220°F.

The reaction taking place in the slaker and causticizers may be represented as follows:

$$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3$$

Sodium hydroxide is the active cooking agent along with sodium sulphide which remains unchanged throughout causticization.

The white liquor (Fig. 5) passes into decanters which are cone-bottomed steel tanks fitted with four chains that scrape along the cone at 3 revolutions per hour. Sludge is withdrawn from the bottom, and the clear

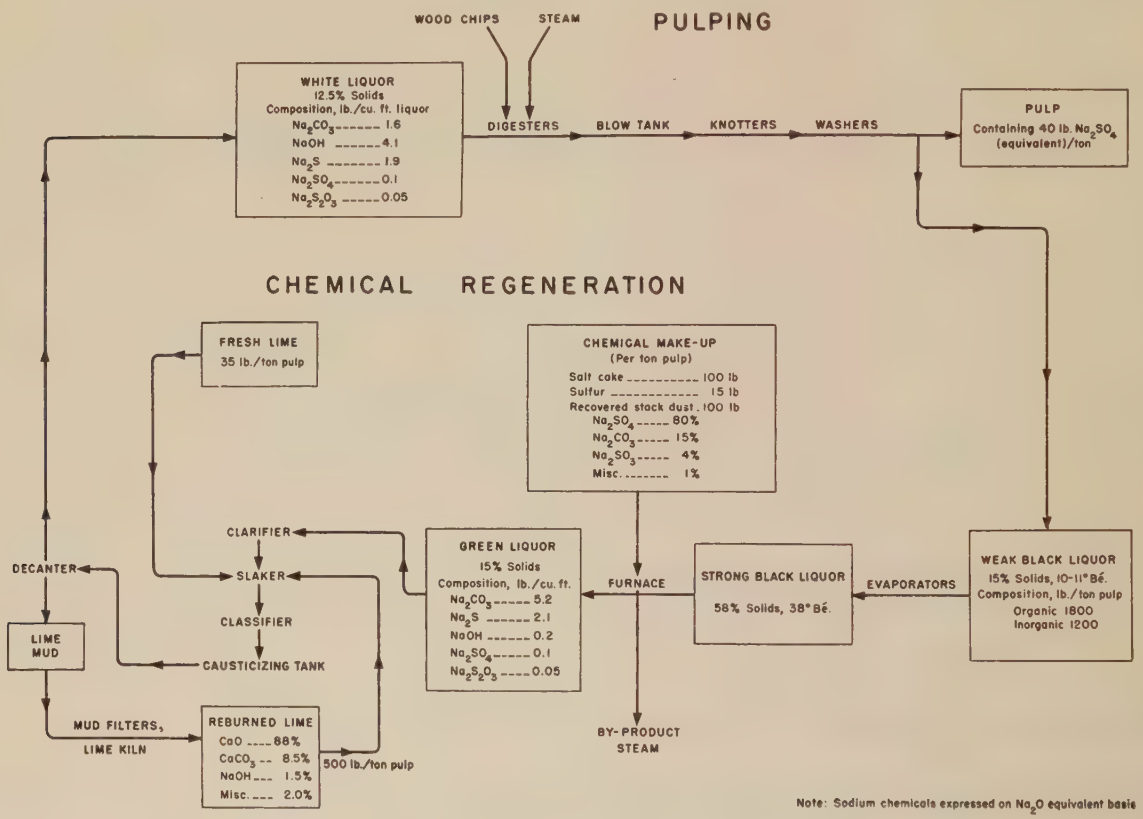

Fig. 5. Chemical recovery cycle

liquid being pumped) and other impurities settle out. The sludge is washed and the dregs dumped; the wash is returned to the dissolving tank, and the green liquor overflows the clarifier and flows by gravity to storage (Fig. 4).

Lime and green liquor (about half that needed to complete the reaction) are added together at the feed end of a rotating slaker (*8E*) which is 20 feet long, 5 feet in diameter, and turns at 15 r.p.m. The slaked lime exists at the discharge end at the boiling point and flows to a classifier (*9E*) where all the underburned and overburned cores from the lime-kiln operation are removed along with any sand and other foreign matter. The milk of lime slurry is then pumped to steel causticizing tanks, 12 feet high and 12 feet in diameter, agitated by a steel paddle on a central shaft rotating at 20 r.p.m. Here the balance of the green liquor is added. The white liquor overflows into storage tanks; it is then pumped to the digesters as needed.

Green liquor, prior to complete causticization, tends to form scale on the inside of pipes, tanks, pumps, and fittings. These must be cleaned every 6 months by mechanical reaming. The main constituent of green liquor scale is sodium carbonate; after lime addition at the slaker it is calcium carbonate. Where green liquor is handled there is increasing use of stainless steel. Between the causticizing tanks and the decanter, pumps and piping are made of stainless steel Type 304.

Above 200°F. or in the presence of agitation, or both, any caustic solution is corrosive and stainless steel is desirable, but the high cost limits its use. Ordinary steel is used after the decanter. Although temperatures are above the critical point in the digester, the caustic concentration is low enough because of steam

LOBDELL GHV ROLL GRINDER

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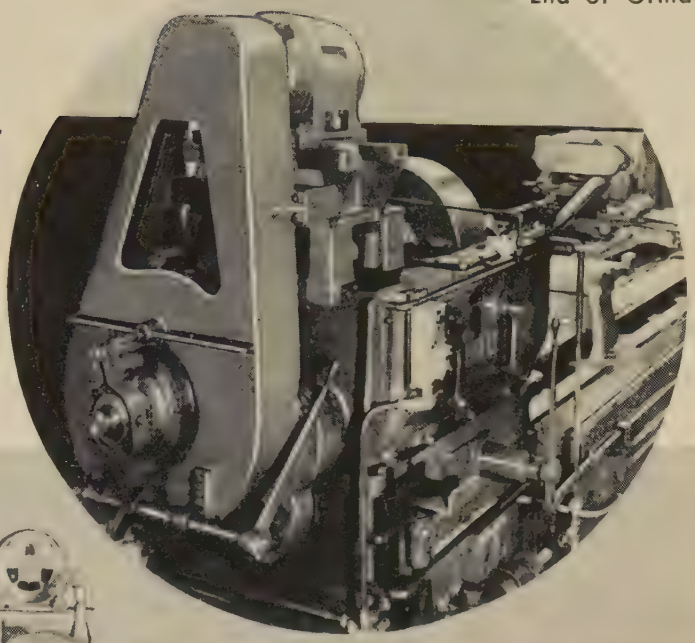
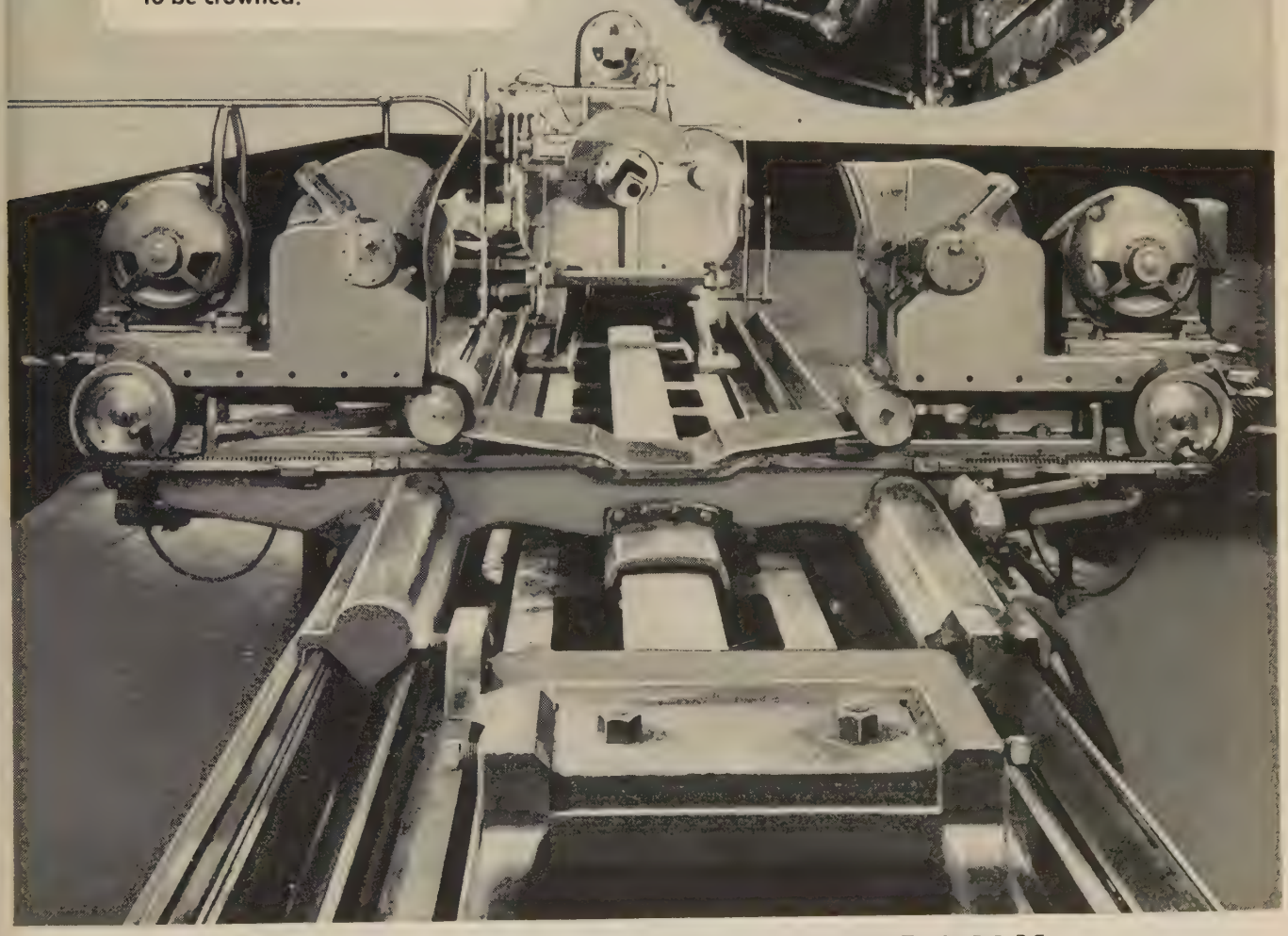
Close-up of Drive End of Grinder.



No. 5 GHV Lobdell Roll Grinder, with a roll size capacity of 8″ to 44″ diameter and 270″ face.

Was installed in 1949.

Not shown, but supplied with this machine is an auxiliary extension mechanism which enables rolls 60″ in diameter to be crowned.



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addition and reaction with wood so that ordinary steel gives satisfactory service. The stainless steel linings in six of the digesters have not been in use long enough to determine accurately their life.

LIME KILN

Lime sludge is withdrawn from the bottom of the decanters by pumps and sent to two vacuum filters (*12E*) in series (6 feet in diameter with 4-foot face). In the primary washer, filtrate from the secondary stage is used as wash liquor, and fresh water is used on the secondary stage. Sludge from the secondary stage drops on a screw conveyer which transfers it to the cool or feed end of an oil-fired rotary kiln (*2E*), 120 feet long and 8 feet inside diameter.

As the kiln rotates at 0.5 r.p.m., the sludge gradually moves through a chained section, then down to the front of the kiln, being "burned" by the intense heat. It finally emerges as "reburned" lime which is used again for causticizing. This lime recovery is essential to economical operation. In the early days of kraft pulping, the sludge was dumped and new lime used. Without recovery, lime usage would be 500 pounds per ton of pulp. With recovery, lime make-up averages 30 pounds per ton of pulp.

Kiln operation is controlled by a radiation pyrometer (*6E*) in the hot or discharge end (2100 to 2300°F.) and a recording thermometer (*11E*) at the cool or feed end (400 to 600°F.). A recording conductivity meter on the filtrate from the sludge filters gives the amount of soda left in the cake going to the kiln. It is important that this be kept between certain limits; otherwise, "ringing" occurs. This is caused by the tendency of lime sludge entering the kiln to stick to the walls in the form of rings which prevent the free passage of lime. Before installation of slaking and classifying equipment, much trouble was experienced. This has been licked by providing clean lime sludge, free of underburned lime, overburned cores, and other foreign matter.

Reaction occurring in the kiln is represented as follows:

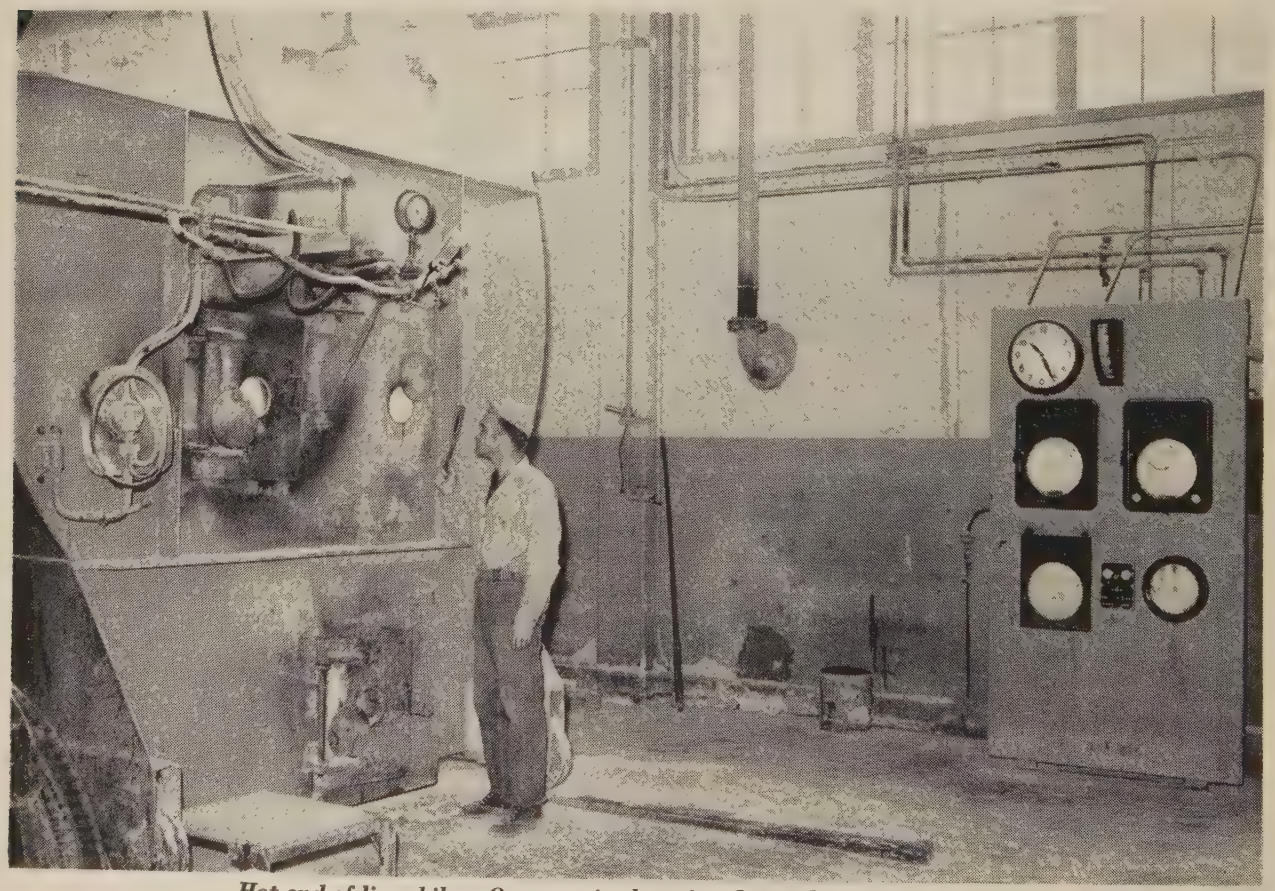
$$CaCO_3 + \text{Heat} \rightarrow CaO + CO_2$$

At least 90 to 95% of the lime used in causticizing is recovered through the kiln and reused. The balance of usage is made up with new lime.

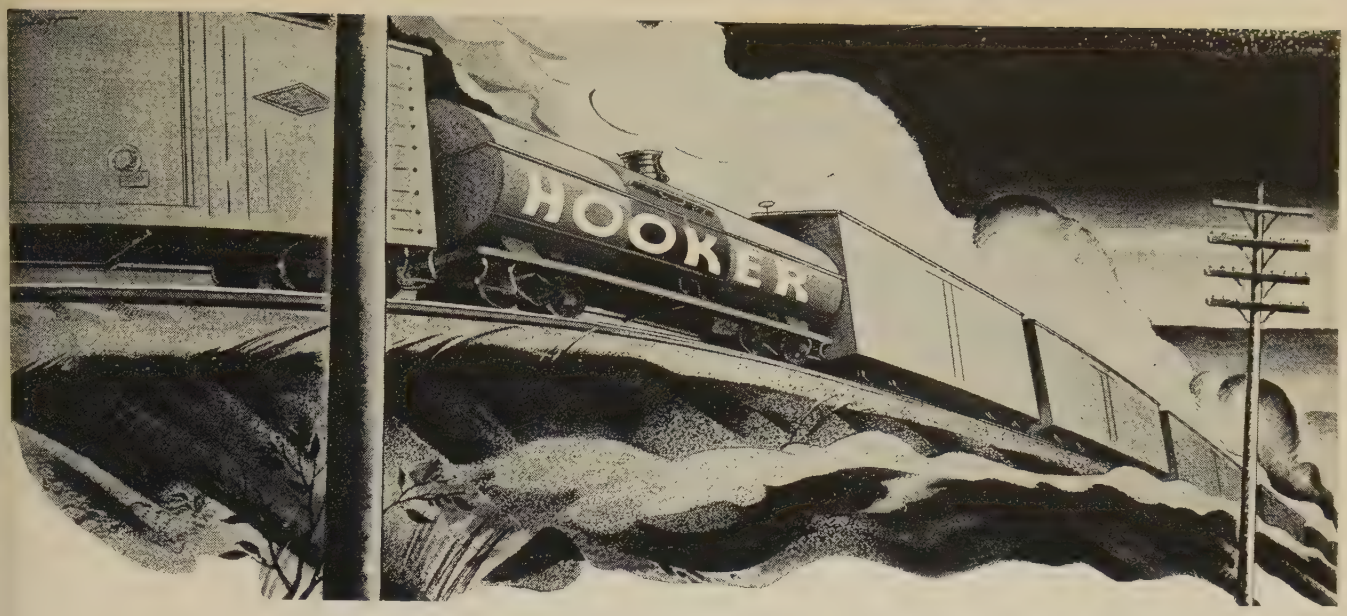
It can be concluded that the manufacture of kraft pulp is largely a chemical recovery process. The recovery efficiency must be over 80% and with modern equipment should be about 90%.

This is accomplished with a low labor requirement. Only 1.5 man-hours are necessary to make 1 ton of pulp, air-dry basis. For a typical 330-ton day there will be 17 men in production on three 8-hour shifts, totaling 408 man-hours. To this are added: maintenance, 35 man-hours; laboratory, 16; supervision, 16; engineering, 12; and inspection, 8. All men work on a 5-day, 40-hour week.

A further breakdown shows that digestion and screening require two cooks, four helpers, and two men on screens and washers. The evaporators and Cottrell require one man; four men take care of the two recovery furnaces; one boilerman tends both units; and one man handles the chemicals. For the remainder of the process, one man is in charge of the sludge filters



Hot end of lime kiln. Operator is observing flame through cobalt glass



Liquid Chlorine Versus Bleaching Powder

ALTHOUGH bleaching powder was in regular use by pulp and paper makers for many years, it carried with it time consuming and costly difficulties. Bleaching powder was never stable in storage and when made into bleach liquor, it was difficult to get clear solutions and to eliminate sludge.

When liquid chlorine became readily and cheaply available, the old bleach powder methods could be discarded. Under the stimulus of production for World War I, electrolytic cell design improved, chlorine production increased and economical methods of liquifying and transporting were developed. Hooker engineers and chemists played an important part in this progress. They also helped specifically in the pulp and paper industry not only in improving bleaching techniques but in the designing of bleaching equipment.

Hooker technicians are constantly engaged in making available for you the high purity liquid chlorine and other Hooker chemicals you use. The results of their studies, too, are available in Hooker Technical Bulletins and cover a wide range of subjects of interest to pulp and paper makers. A list of the titles of these bulletins and copies of those you would like to have will be sent to you when requested on your letterhead.

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and lime kiln and one man makes the caustic liquor. On each shift there are also a foreman and a pulp tester. One shift a day includes a laboratory tester, six maintenance men, a cleanup man, and an electrician. For special tests there may be an additional laboratory tester. There is also part-time service available from the general mill labor resources. Inspection is called "preventive maintenance" and is planned so that shutdown of equipment can be done on schedule instead of only in emergencies.

THE FUTURE

The Douglas-fir region of the Pacific Northwest and the southern pine area of the Southeast are the two largest remaining sources of wood in the United States. It is natural to expect that the future of the pulp and paper industry will loom large in the economy of those regions.

The rapid growth in demand for kraft pulp shows no sign of slowing down. More sources of pulp will have to be found. These may result from improved wood waste harvesting, utilizing low grade wood and the less preferred species, and increasing pulp yields.

Statistically, there is enough suitable wood as saw mill waste, windfall, and logging waste in the area bounded by California, the Cascades, and Canada to more than supply all the needs of the pulp and paper industry of the area. Present economics militate against salvaging this wood because it is found in scattered and isolated locations.

New uses for kraft pulp will also be found. An example is the recent use of kraft for dissolving or nitrating. This had been impossible for years because of the noncellulosic impurities. During the past 10 years, German pulp technologists were able to prepare kraft pulp suitable for those purposes through a mild prehydrolysis with sulphuric acid. This opens up a new field for kraft pulp because the dissolving pulps constitute an increasing market as rayon consumption soars.

During the past 40 years the kraft process has been improved largely by refinement. In 1950 the fundamental process remains the same but costs have been cut, chemical recovery is more efficient, and the product is better because of controlled manufacturing conditions maintained through dependence on instrumentation instead of manual control. These and many more changes have all contributed to the conservation of our disappearing natural resource, wood. But these changes are not enough to ensure a vastly expanded future for the industry. The reason is based on fundamental wood chemistry.

The natural material comprises about 52% α-cellulose, 28% lignin, 15% hemicelluloses, and the remaining 5%, rosins, fats, and extractives. In removing the bulk of the lignin of wood from a pulp, nearly one third of the cellulose is lost since only about 37% of the original wood is recovered in a good kraft pulp as α-cellulose. A summation of all the remaining possible refinements of method will not provide means for recovering all the α-cellulose. Since the aim in pulp making is to retain all of it that was present in the original wood, future developments must be based on some radically new approach. Economics demand it, since the cost increases as wood reserves are depleted.

Perhaps more important from a natural resource standpoint is the utilization of the noncellulosic part of wood. The most abundant unexploited organic byproduct in the world today is lignin which comprises about 30% of the weight of wood. In the manufacture of pulp by the alkaline processes, only heat is reclaimed from the lignin in the burned liquors. Few chemical uses have been found. These include: paper impregnant, molding powder, expander in lead-acid batteries, the ethers as film formers in protective coatings, the stearate as a mold lubricant, dispersing agent in asphalt emulsions, base exchange material, and a few other minor uses (*4*)

The market for any one of these uses could probably be satisfied by the output of one mill. The production of heat is the only current large scale use of lignin. This is a low grade of economic recovery and should be replaced by more profitable chemical products. There are 4,000,000 to 5,000,000 tons of lignin available each year in the United States from pulping processes. This is the incentive for a large and expanding field of research.

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11. *Pulp and Paper*, 23, No. 5, 103 (1949).
12. *Pulp and Paper*, 23, No. 5, 104 (1949).

PROCESSING EQUIPMENT

1E. Allis-Chalmers Mfg. Co., Milwaukee 1, Wis., *Bull.* 07B6353, low-head horizontal-type flat deck vibrating chip screens.
2E. Allis-Chalmers Mfg. Co., *Bull.* 07B6368, lime kiln.
3E. Allis-Chalmers Mfg. Co., *Bull.* 07B6592, high-density knotter screens.
4E. Babcock and Wilcox Co., New York 6, N. Y., *Bull.* 3-268 (1940); *Bull.* P-1 (1946); *Bull.* 3-415 (1948), Tomlinson recovery furnace.
5E. Babcock and Wilcox Co., rotary digesters.
6E. Brown Instrument Co., Philadelphia 44, Pa., radiation pyrometer on lime kiln.
7E. Dorr Co., New York 22, N. Y., green liquor clarifier.
8E. Dorr Co., Kilby lime slaker.
9E. Dorr Co., slaker-classifier.
10E. Foxboro Co., Foxboro, Mass., *Bull.* 348, time-cycle pressure controls for digester.
11E. Foxboro Co., recording thermometer on lime kiln.
12E. Oliver United Filters, Inc., New York 18, N. Y., *Bull.* 216, vacuum sludge filter.
13E. Sumner Iron Works, Everett, Wash., Bellingham type hydraulic barker with Crown Zellerbach modifications.
14E. Sumner Iron Works, two-anvil chipper, 6-knife, 153-inch diameter.
15E. Swenson Evaporator Co., Harvey, Ill., *Bull.* E-100, sextuple-effect evaporators.
16E. Swenson Evaporator Co., *Bull.* F-104, 2-drum 4-stage Swenson-Nyman pulp washer.
17E. Swenson Evaporator Co., digester blow heat recovery system.
18E. Western Precipitation Corp., Los Angeles 15, Calif., Cottrell electrostatic precipitators.

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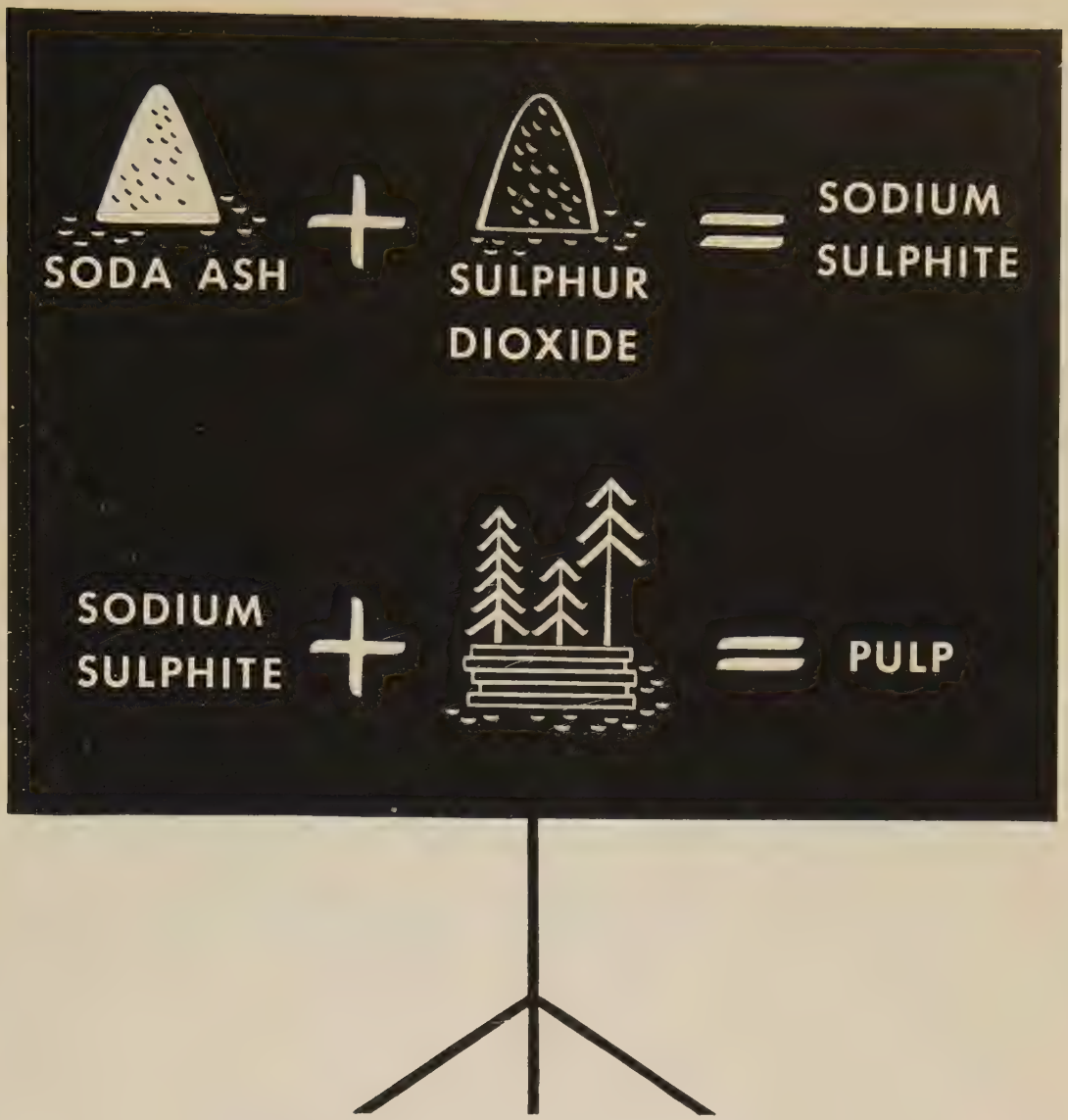

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Industrial Use of Ground Water

W. F. GUYTON

The United States Geological Survey, or the USGS as it is called, is the primary Federal agency designated by Congress to make basic investigations of the Nation's water resources. No construction, development, or operation of water supplies is involved in its work, but only studies to determine the occurrence, quantity, and quality of ground and surface waters. Most of these studies are made in cooperation with state and local governmental agencies in areas chosen because of the need for the studies and the amount of good they will do for the public. During the war, investigations were made for war agencies that directly benefited private industries with war contracts, but now, as before the war, regulations do not allow work for individuals or private concerns. The USGS is always happy, of course, to furnish all the information it can from its files to anyone, but each field project must be given careful scrutiny before it is undertaken.

On the other hand, there are a number of well-qualified consulting engineers and geologists who do make private investigations and who, in the process, take full advantage of the more general studies that the USGS makes. Furthermore, there are many state and local agencies that can furnish help of one kind or another, and many well drillers have accumulated a surprisingly large amount of data and have a sound practical knowledge of the ground-water resources of their areas.

Accordingly, when a private industry needs help in determining how much ground water is available and what the quality is, it can turn to any one or to all of the several sources of help. The USGS and the other agencies can usually provide much good information about ground-water conditions in general in the area involved, and the drilling contractor can furnish much information about the various types of wells and the methods and costs of constructing them. Finally, the engineer can take this information, interpret it in the interests of the particular industry, make additional investigations where necessary, and then recommend the wisest procedures to follow in constructing, developing, and operating the water supply.

Recently the press and radio have been full of items concerning the water shortage in New York, and the corresponding problems in other parts of the country. Some of the pieces have been purely factual with little interpretation as to what is going to be the outcome of it all. Others have given the impression that the water supplies, and particularly the ground-water supplies, are being mined and depleted at an excessive rate and that in a few years we will have used up our valuable ground-water resources and will be in dire straits.

The truth is that there is no such thing as a nation-wide depletion or shortage of ground water. Ground water is a replenishable resource, and in most of the country there is still a lot to spare that percolates unused into streams and into the oceans, or evaporates into the air.

There are, however, a good many places where problems have been created because users have attempted to take too much water from too small an area. As the storage has been used up, the supplies in these areas have been limited to the perennial recharge, and shortages have occurred because the recharge is not sufficient to meet all demands. Some of these shortages cannot be met economically by importation of water, and curtailment of existing industrial and agricultural development is in prospect. In a few such places, widespread areas are involved.

W. F. Guyton, Hydraulic Engineer, U. S. Geological Survey, Washington, D. C. (In accordance with the Geological Survey's usual procedure, this paper has been reviewed and contributed to by other members of the Survey, and has been given the Director's permission for publication.)

In other places, however, additional water is available, though at increased cost, and the problem is simply to obtain it in the best and cheapest way. Naturally, as the cost of the water is increased, the people who are paying the bills are beginning to sit up and take notice, and in some cases are beginning to cry "water shortage." It must be realized, though, that ground water cannot be obtained without some decline in water levels to cause the water to flow toward the wells, and a decline always means, of course, an increase in pumping lift. It is in the places where the pumping is so great that the water levels will not stop declining before reaching excessive depths, or where the water levels cannot possibly stop declining with the existing pumping rates, or where development of ground water adversely affects surface-water rights on streams to which it is tributary, that the really serious problems occur.

Instead of being faced with the national problem of reducing ground-water use, the problem is, rather, one of distributing the use so that overdevelopment of local areas can be eliminated or kept to a minimum, and so that better advantage can be taken of the ground water that is now wasted by return to the atmosphere or by passing unused on its way to streams and thence to the sea.

It is estimated by the Weather Bureau that an average of about 30 inches of precipitation occurs annually over the United States. Of this amount the USGS records show that about $21\frac{1}{2}$ inches soon goes back into the atmosphere as evapotranspiration and $8\frac{1}{2}$ inches runs off directly through streams, or through the ground and thence through streams, to the oceans. Roughly three quarters of an inch is estimated by the USGS to be intercepted by water users throughout the country, who use in the order of magnitude of 100 to 200 billion gallons a day.

About 25 billion gallons a day is taken from the ground through wells. This is something like twice as much as was used from wells 10 to 15 years ago, and nearly 5 billion gallons a day more than the use in 1945.

The 25 billion gallons may be divided roughly as follows:

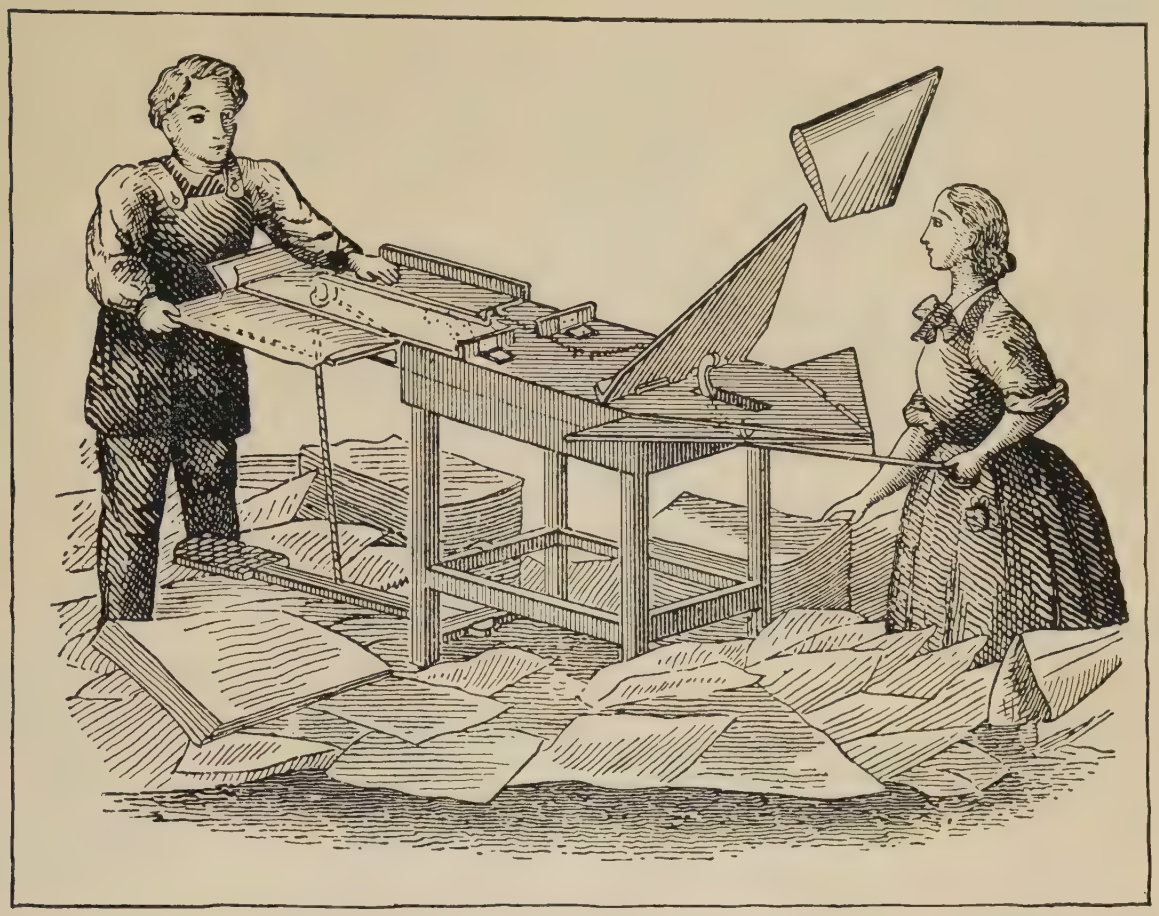
	Billion gallons per day
Irrigation	15
Industrial (not including water from municipal systems)	5
Municipal	3
Rural (not including irrigation)	2

During the war, the use by industries increased more, proportionately, than other uses, but since the war there appears to have been a somewhat larger increase for irrigation than for other purposes.

The USGS doesn't attempt to keep records of the cost of water, but the author's impression is that about 5 cents a thousand gallons is a reasonable figure for industries that use fairly large quantities. Some paper mills operate on less than that amount, but a lot of other smaller users pay considerably more. Figured on the 5-cent basis, the cost of ground water to industries in the country is about a quarter of a million dollars a day which is a sizable amount. Bringing this down to a single large paper mill which might use 10 to 20 million gallons a day, the cost would be $500 to $1000 a day. The author does not know whether these cost figures are average or not, but at least they seem in the correct order of magnitude and give an idea as to the importance of the water supply to a mill.

Many industries prefer ground-water supplies to surface-water supplies, for a variety of reasons. A few of these reasons might be given. For instance,

1. Ground water is available in many places remote from streams or lakes, or from municipal supplies.
2. The costs of development, operation, and maintenance of ground-water supplies in many places are lower than the corre-



Hand-Operated Bag Machine, about 1835. Illustration from the Bettmann Archive

The Bag Business is Big Business

One hundred sixty years ago, inventors were trying to devise a machine that would shape and fasten a piece of paper to form a paper bag. Hand-operated machines were built about 1835. Then in 1852 Francis Wolle, of Bethlehem, Pennsylvania, patented the first automatic bag-making machine. In 1858 he produced an improved machine which made bags from a running roll of paper, cutting, folding, and pasting in a continuous series of operations. Great modern machines now turn out millions of bags a day, serving the infinite packaging needs of business. Working their miracles, they form every type and size of bag from tiny glassine containers to giant lined bags that hold and protect precious chemicals. So great is the volume that manufacturers of bags and shipping sacks use more than one million tons of paper each year and play an important part in America's great pulp and paper industry.

The dramatic story of paper is told in the sound-and-color film, "Paper — Pacemaker of Progress," and in a book under the same title. Both are presented by F. C. Huyck & Sons as a tribute to the Paper Industry. The book will be sent free upon request.

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sponding costs of surface supplies. This is especially true for supplies of small to moderate size in which impoundment and treatment of surface water would be required.

3. Ground water is nearly always constant or fairly constant in temperature; the temperature ranging from mean annual air temperature to several degrees higher, depending on the depth of the wells. Industrial cooling equipment can be more efficiently designed for constant temperatures than for fluctuating temperatures. Also, many industries require cooling water lower in temperature than the temperature of surface water during the summer, and ground water during this period is usually about 10 to 30° cooler than surface water during the summer.

4. Ground water also has a fairly constant mineral content, whereas the quality of water from streams is apt to vary with changes in flow. This is particularly important to some industries such as paper mills, bottling works, and the like where the water enters into the process. However, ground water is generally somewhat more highly mineralized than surface water, and this tends to offset the advantage resulting from its constant quality.

5. Rarely is there a need to treat ground water to remove suspended matter and only occasionally is there a need to sterilize it.

6. There have been many cases where pure water supplies have been developed and later have become contaminated from wastes of one kind or another. This is less likely to occur to ground-water supplies than to surface-water supplies.

7. There are not as many laws pertaining to ground water as to surface water, which allows more new industries to "enter into competition" for ground water than for surface water, for the earlier users have not been granted prior rights as universally as in the case of surface water.

Some may think of other reasons why particular industries want ground water in preference to surface water, but doubtless you also have already thought of reasons why surface-water supplies are more feasible in some cases. Some of these are:

1. In many places there is not enough ground water for large users. In other words, the water-bearing formations at particular locations aren't productive enough.

2. There generally is somewhat more uncertainty as to the availability and continuing supply of ground water, though sometimes the reverse is true, especially in the more arid regions.

3. Fewer engineers who plan water-supply developments understand ground-water hydrology. This is partly because of a lack of knowledge of geology, but also because of a lack of knowledge of ground-water hydraulics.

4. Ground water has a bad name from past failures and overdevelopments caused by this lack of knowledge.

5. In some places, instead of having a low cost of development, ground water has an extremely high cost of development resulting from geologic or man-made conditions of one kind or another.

6. As already pointed out, ground water generally has a higher mineral content than surface water.

7. New ground-water developments are more likely to be able to rob existing supplies, or at least increase their cost, than in the case of surface water. This is partly due to the nature of ground-water occurrence and partly to the scarcity of laws pertaining to ground water.

Some of these reasons discouraging the use of ground water are disappearing, or should disappear, though. As time goes on and knowledge increases, it is becoming increasingly difficult to justify or excuse haphazard development, overdevelopment, and failure of ground-water supplies. Ground-water hydrology has now matured into a full-fledged science, the same as surface-water hydrology, or the hydraulics of flow through pipes.

Within reasonable limits and on the basis of adequate investigations, the hydrologist now can predict the yields and drawdowns of water levels that might be expected at any time after a given development is made. Interference with existing supplies can be predicted, and possibilities of increasing supplies with artificial recharge and induced infiltration can be determined. Future changes in the quality of water can be predicted.

The crying need in the past has been for such investigations and predictions. More often than not, no studies have been made until troubles have arisen. Then it is a question of doing the best thing possible to correct the situation. It often costs many thousands and even millions of dollars to do so, whereas the problems could have been anticipated and largely forestalled if adequate information had been available and the proper types of development could have been made in the beginning.

WATER SHORTAGES CAUSED BY INADEQUATE DATA

Take the case of Louisville, Ky., for example. For a short period in 1943 the pumpage from wells for war industries reached a peak of about 75 million gallons a day. Before the war it was only about 37 million. The water levels between 1940 and 1943 had dropped so much that the yields of some wells had decreased to a quarter of their original amount, and in 1943 in the rubber-manufacturing district there appeared to be less than a 2-year supply left in the ground-water reservoir. Under the pressure of the war emergency, it had been necessary to make all the new developments without prior investigation of the ground-water reservoir, its natural recharge, its permeability, and other essential hydrologic and geologic factors. When the Geological Survey was called in to help with the problem, it was able to map the reservoir and to determine the sources and amounts of recharge. It was found that the recharge, under the existing conditions of development, was only about 40 million gallons a day. Therefore, it was necessary for the industries to take action in a hurry, and they did. The use of water was decreased by means of cooling towers, recirculation, and other water-saving measures, and some industries began to buy water from the City which draws directly from the Ohio River. Others relocated their wells closer to the river in order to draw in additional recharge, and a few artifically recharged the underground reservoir with city water or with ground water that had been used for cooling. By 1945 the pumpage had been decreased to about 45 million gallons a day, and now it is less than 40 million. The problem was solved, but it has been estimated that the cost of the measures taken to prevent a water shortage was around $5,000,000. The irony of the situation is this—the Geological Survey's investigations, begun during the war and continued since then, have shown conclusively that several hundred million gallons a day of cool ground water can be obtained by locating wells along the Ohio River to the north and south of the city, where the water can be made to infiltrate from the river at high rates. Had this information been available before the war emergency came, the large water-supply developments that it was necessary to make in such a hurry probably could have been made without danger of a shortage, and a large part of the $5,000,000 might have been saved.

Another good example of such a problem is Camp Hood, at Killeen, Texas, which might easily have been just a good-sized industry so far as water is concerned. When this tank destroyer training camp was first planned, the USGS was asked about the ground water in the vicinity. The report of the USGS was that there was not a sufficient supply. Unfortunately, however, the Army had to go ahead and build the camp in a hurry at that location, anyway, so it developed a supply 14 miles from the camp by drilling 7 wells about 1000 feet deep, located in a deeply incised valley of a small stream. Small flowing wells that had never failed supplied homes in the valley, and these indicated to the Army that a larger supply might be available. The wells for the camp were equipped with pumps but were designed to flow naturally when not being pumped. A few days after pumping was begun, however, the water levels in the wells dropped below the pump bowls. It was necessary to lower the bowls and lower them again. When the USGS made pumping tests on

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the wells to determine the hydraulic characteristics of the water-bearing formation, it was computed that within the year the water levels could be nearly 300 feet below the ground. Furthermore, the water was found to contain about 1700 p.p.m. of dissolved minerals, mostly Glauber's and Epsom salts. On the basis of these studies, and after operating the wells long enough to see the computations become actuality, the Army finally decided to use the wells for stand-by only and install a surface-water supply. Fortunately, they were able to use the original pipe lines.

Had the results of the pumping tests been available in advance of setting the pumps, the expense of resetting them might have been saved. And, had the results of area-wide water resources studies been available to the Army before the press of the war caused the camp to be built in such a hurry, there might have been time for them to plan and install the surface-water supply in the first place without drilling the wells.

A very important reason for making ground-water investigations that is receiving more and more attention is to furnish the basis for effecting simple economies in everyday developments. Little economies in such things as the selection of proper screens, proper pump settings for future conditions, selection of the most desirable aquifer where there is more than one, proper penetration of well, and the most favorable well spacing can add up very quickly to far more than the cost of the necessary investigation.

A major part of the job before us, therefore, is to find out what the conditions are before developments are installed to permit the most efficient and economical development and to insure against failures due to local overdevelopment.

PLANNED DEVELOPMENT OF SUPPLY

Before the Southland Paper Mill was located at Lufkin, Texas, a rather thorough reconnaissance study was made of the ground-water conditions, and the mill was assured of a supply of about 5 million gallons a day. Five large wells were developed and put into operation in 1939 to yield that amount of water. In 1941, however, the company commenced to think of expanding their plant, and wondered about the water supply. They had kept readings of the water levels in their wells, and the USGS and Texas Board of Water Engineers were keeping records of water levels in the surrounding area. Unfortunately, the water levels were still declining as a result of the beginning of their 5-m.g.d. pumping, and it was not possible to predict offhand where they would end up. At first, the company was told that probably it would be necessary to run a pipe line about 5 miles away from the existing wells and put in some more wells in order to get another 5 m.g.d. Such a procedure might have cost $200,000 or more. However, they were told that new methods had been developed for computing such things, and the USGS and the Texas Board of Water Engineers would be willing to try them out on an experimental basis on the paper mill wells. Accordingly, a series of pumping tests was made on the wells, and the hydraulic characteristics of the water-bearing formation were determined. This information was applied, by use of the USGS methods, to computing future water levels. It was found that, if the existing pumping rates remained the same, the water levels would very soon stop declining, for all practical purposes, and that if the pumping rates from the five wells were doubled, the water levels would decline as much again as they had already declined, but no more. The figures and methods were checked and double-checked, and no slip-ups appeared. So, after studying the pump capacities, bearing strengths, sand production of the wells, and other such things, the company decided to obtain their additional 5 m.g.d. needed by simply lowering the pump bowls and doubling the pumping rates in the existing wells. A safety factor of 25% was allowed in the computations for new pump settings, and the project was undertaken.

The company set up an elaborate system to watch the water levels, not only in their own wells, but also in wells throughout the area. An accurate record was also kept of all other pumping in the area.

After about a year of operation at the new rates, the computations were remade using the actual pumping rates, and the method of predicting was found to yield results about 5% off for the pumping levels in the five wells.

In 1948 the mill's pumping was increased again, but this time the wells did not have enough remaining capacity, so it was necessary to put in a pipe line and some new wells.

This is an example of a highly efficient paper mill staff taking full advantage of available information on the water resources, adding to it, and using the most scientific methods of designing, developing, and operating their water supply. Large amounts of money and critical material were saved by their doing so. If more industries, municipalities, and irrigators operated in this manner, our trouble-shooting days would soon reach an end.

The USGS is doing its best to make this possible by obtaining good data on the ground water throughout the country. There is a tremendous amount of work to be done, though, and so far only a small percentage of the country has been investigated adequately. Considerable information is available in much of the unexplored area, but not enough for the kind of planning an industry or other user needs to make for a new water supply or for a major increase in an existing supply.

For instance, we know that large supplies exist in many places, but not exactly how much. A couple of years ago a paper manufacturing concern came to the USGS with a request for a list of areas in the Southeastern and Southern coastal plains where a supply of 30 million gallons a day could be readily obtained. Only a few could be named, and for most of the sites subsequently considered by the company, it could only be said that there was a possibility of obtaining the water, but that any development must be preceded by a general ground-water investigation to determine the facts. Unfortunately, experiences of this nature are rather common.

However, such will not always be the case. Though it has taken 60 years to accumulate the data now available on ground water, an equivalent amount of additional data will be obtained in a much shorter time in the future. Congress has increased the work of the Geological Survey several fold in the last 10 years, and there is indication that still more increase is contemplated. The multitude of water-supply problems has aroused many Federal and State legislators and others to the need for action, and a very wide movement is now under way to make adequate investigations of the Nation's water resources and to develop and conserve them in an intelligent and orderly fashion. Conservation associations, contractors, engineers, and water users are all supporting this movement. As it gains in momentum, the basic data on water resources will be obtained, and proper conservation and regulatory measures will be put into effect.

The other half of the job then will be primarily up to the water users, such as the paper mills. Rule-of-thumb methods, guesses, and witchcraft must go out of practice. Negligence and carelessness must not be tolerated. The investigation, development, and operation of ground-water supplies must be recognized as a scientific and engineering procedure to be conducted according to the highest standards of the profession, the same as other technological phases of an industry.

When this is being done, and the basic data are collected, the future of ground-water developments will be very bright indeed. The tremendous undeveloped supplies of the country will be wisely and efficiently utilized by our expanding national economy, and the days of water shortages caused by faulty planning will no longer exist.

Presented at the Annual Meeting of the Technical Association of the Pulp and Paper Industry, New York, N. Y., Feb. 20–23, 1950.

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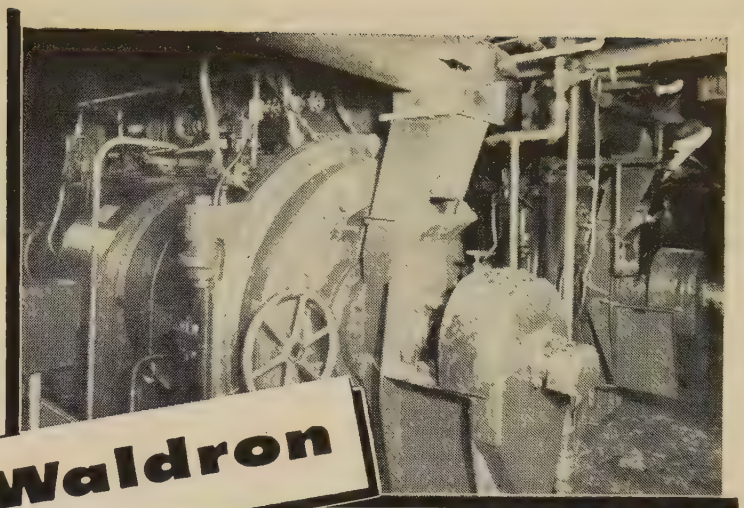

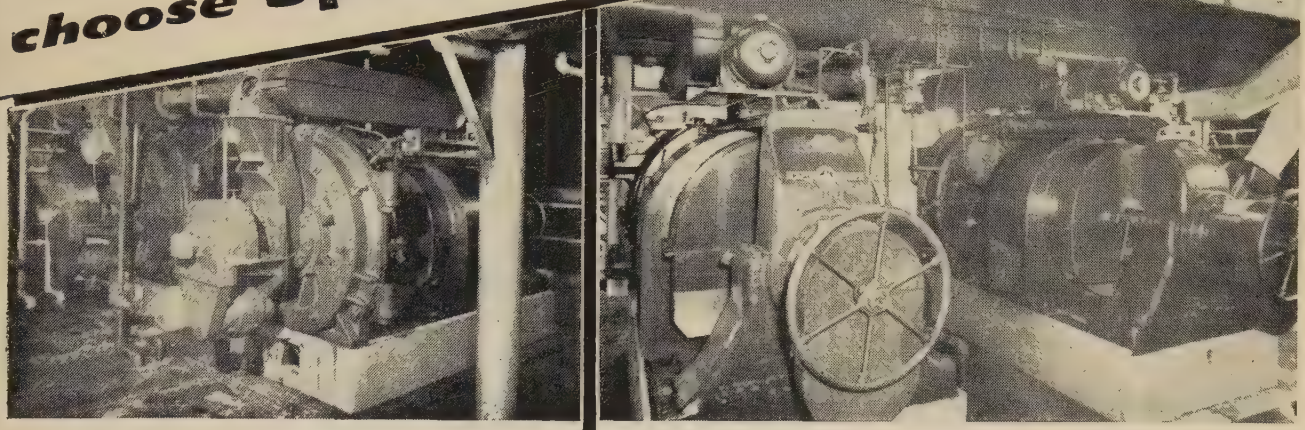

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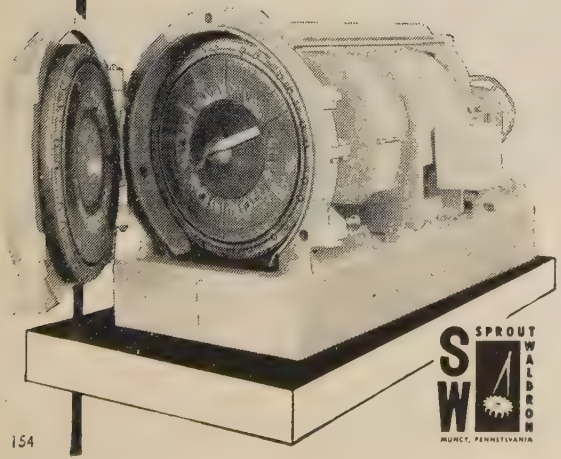

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Improved Straw Pulp for Corrugating Paper

H. M. SUTCLIFFE, S. I. ARONOVSKY, R. M. WILKINSON, W. D. BURNHAM, W. A. PHILLIPS and E. R. CARPENTER

A large number of experimental cooks were made on wheat straw varying the amounts and kinds of chemicals in an attempt to produce improved pulps for corrugating. This work was part of a cooperative program between the strawboard industry and the Northern Laboratory and was carried on with the active collaboration of personnel from several strawboard mills. The chemicals used were lime, caustic soda, sodium sulphite, singly and in various combinations. The pulps prepared with caustic soda or sodium sulphite and with combinations of these two chemicals were distinctly stronger than lime-cooked pulps. The optimum results in this series of experiments were obtained with 6% NaOH, 10% Na_2SO_3 2% NaOH plus 4% Na_2SO_3, and 2% Na_2SO_3 plus 4% Na_2CO_3. The results indicated that suitable refining of straw pulp may be fully as important as the method used in preparing the pulp. Because of its high hemicellulose content, straw pulp is an excellent material for producing corrugating paper with high-crush resistance. The results of this work offers the operating strawboard mills a wide latitude in choice of cooking chemical to produce the desired improved product consistent with the variation in methods and equipment used in each mill.

MANY changes have taken place in the picture of strawboard production in recent years. Straw stacks on the farms have practically disappeared. The straw procurement and baling season has been compressed to a period of about 2 months. The apparent shortage of straw during the war years has been overcome by increased availability of relatively low-cost, one-man baling machines—most mills now obtain their major straw requirements within a 25 to 75 mile radius.

With the raw material problems well on the way toward solution, attention was turned to methods for improving the quality of straw pulp and of the resulting strawboard. Many mills experimented with sodium sulphite as a pulping agent for straw. This chemical is now available at reasonable cost as a by-product of the chemical industry. The results, although indicating some improvement in pulp quality, were inconclusive because of the variety of cooking conditions and pulp processing methods used in the different mills.

At a meeting held at the Northern Regional Laboratory in Peoria, Ill., in November, 1948, representative technical men and operators of the strawboard industry developed, in collaboration with the Laboratory staff, a broad program aimed at improving the quality of straw pulp and its processing into strawboard.

A survey of pulping and pulp processing methods and equipment of the various mills was made immediately. Samples of straw pulp, paper furnish, and finished paper were obtained from the mills and evaluated under standard conditions at the Laboratory.

The first experimental phase of this program dealt with evaluation of the several chemicals used in the industry for pulping. Although newer pulping methods appeared suitable for this work (*1*) pressure pulping was used in this phase because it offered an opportunity to translate any promising techniques more quickly to commercial operation with available mill equipment. Several mills participated actively in this program by sending men to the Laboratory to aid in the experimental work. This report describes these pulping studies.

EXPERIMENTAL

Raw Materials

The raw material used was straw from combined, soft winter wheat (Kawvale variety) from the 1945 crop grown in central Illinois. The straw was bright, sound, and relatively free from chaff.

Chemicals

Lime, caustic soda, sodium sulphite, and soda ash were used alone, and in combination, as pulping agents. The percentages indicated in this report refer to the chemicals, used as such, and based on the weight of moisture-free straw.

Pulp Preparation

Since the object of the study was the evaluation of the chemicals as pulping agents, all other conditions of cooking, defibering, washing, and testing were held constant. The whole straw, taken directly from the bale, was cooked with the chemical for 5 hours at 140° C. (40 p.s.i.) with indirect heating. The ratio of dry straw to total liquid was 1:7. The methods of cooking, defibering, and washing have been given in detail previously (*2*).

Testing

Beating and strength evaluation of the pulps was carried out in accordance with the standard TAPPI methods, with one modification. To obtain sufficient pulp for the number of 3-gram sheets (25 × 40—500,120 pounds) required, 1850 grams of the pulp slurry was removed from the standard laboratory beater at each interval instead of the usual 800 grams (T 200 m-45). Preliminary tests had shown that removal of the larger quantities of pulp had no appreciable effects on the test results except to reduce the total number of intervals for obtaining samples in the beater run.

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R. M. WILKINSON, Chemist, Alton Box Board Co., Alton, Ill.; W. D. BURNHAM, Engineer, Central Fibre Products Co., Quincy, Ill.; W. A. PHILLIPS, Engineer, Terre Haute Paper Co., Terre Haute, Ind.; and E. R. CARPENTER, Chemist, Terre Haute Paper Co., Terre Haute, Ind., were collaborators from the respective companies in this work at the Northern Regional Research Laboratory, Peoria, Ill.

The results obtained from 85 cooks are summarized in Figs. 1 to 5. Many of the cooks were made in duplicate, and most of the test results are the means of check beater runs.

RESULTS AND DISCUSSION

Single Chemicals

Lime. Until recently, lime has been the major pulping chemical in most strawboard mills, and the

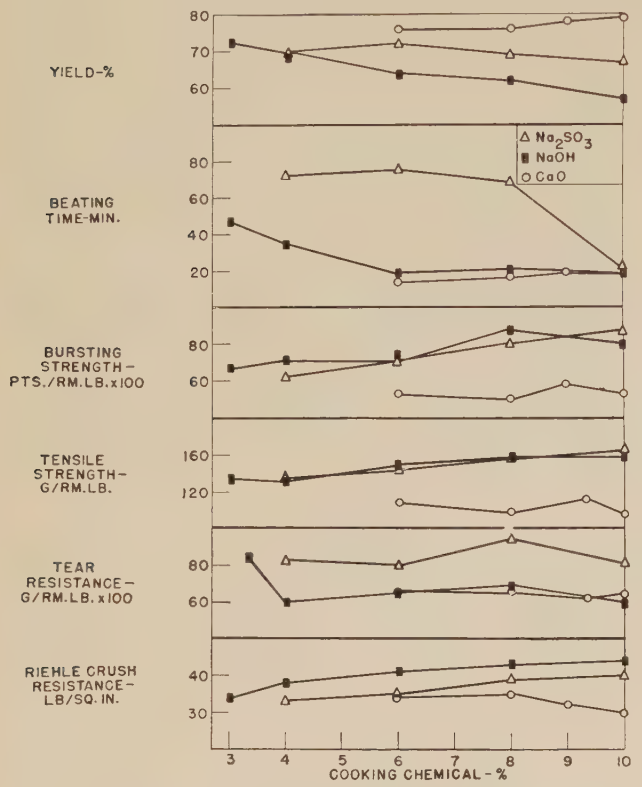

Fig. 1. Effect of concentration of chemicals on yields and properties of corrugating straw pulps

only pulping agent in some. One advantage of lime is its low cost. Another is its relatively low solubility in water resulting in the maintenance of a saturated solution as long as solid lime is available. The main disadvantage of lime lies in the formation of calcium carbonate and other insoluble lime salts which are incompletely removed from the pulped straw in the usual washing practice. Some of these insoluble salts from the pulp find their way into the pores and meshes of the machine felt and wire clothing requiring frequent washups; also the salts remaining in the pulp tend to lower the strength values of the resulting paper.

The yields of the washed, experimental lime-cooked pulps increased slightly with increase of lime from 6 to 10% of the weight of dry straw, as shown in Fig. 1. The increased yields were due largely to the greater inclusion of lime compounds, indicated by the higher ash contents of the pulps. The pulps were relatively soft and easy-beating. The time required to beat to 600 ml. (Schopper-Riegler) freeness varied but little with increase of lime used for pulping; effect on strength characteristics of the pulps, except for a trend toward lower crush resistance was influenced very little by an increase in lime from 6 to 10%. The pH of the waste liquors ranged from 7.5 to 11.6 rising with the increase of lime used for cooking.

Sodium sulphite. Sodium sulphite is gaining favor as a pulping agent in the strawboard industry although not all of the mills agree on the effectiveness of this chemical. It is readily soluble in water and when used for cooking straw, practically no insoluble compounds are formed. Sodium sulphite is a gentler pulping agent than the caustic alkalis, and small amounts of it will thus result in more uniform, even though less thorough, cooking than can be obtained with similar amounts of more active cooking agents. Sodium sulphite is available in anhydrous crystalline form. It costs more than lime, but less than caustic soda.

Smaller yields of experimental pulp were obtained with sodium sulphite than with lime, as indicated in Fig. 1. Increasing the amounts of sodium sulphite from 4 to 10% of the dry straw resulted in only very slight reduction in pulp yield. The relative constancy of yield, however, was not reflected in the beating and strength characteristics of the pulps.

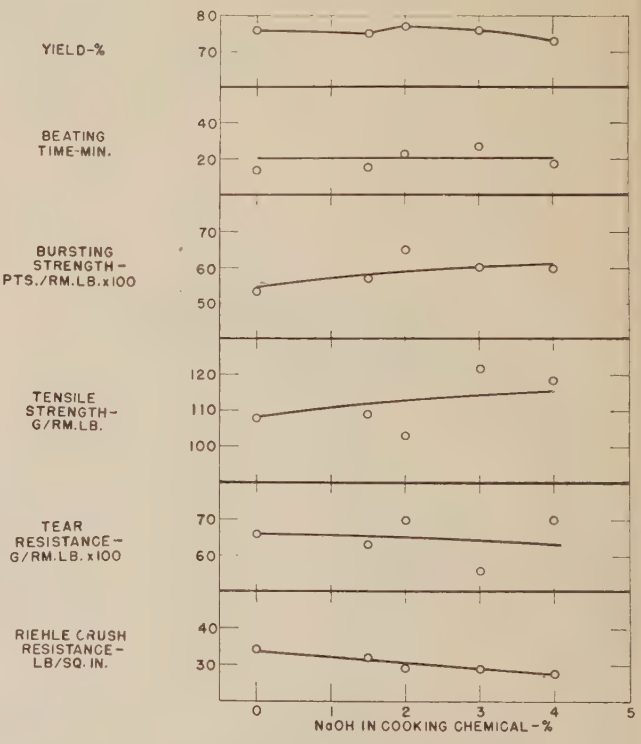
YIELD-%
BEATING TIME-MIN.
BURSTING STRENGTH - PTS./RM.LB.x100
TENSILE STRENGTH - G/RM.LB.
TEAR RESISTANCE - G/RM.LB. x100
RIEHLE CRUSH RESISTANCE - LB/SQ. IN.
NaOH IN COOKING CHEMICAL - %

Fig. 2. Effects of increasing NaOH added to 6.0% CaO in cooking straw for corrugating

Except for the product made with 10% chemical, the sodium sulphite pulps were relatively raw, the degree of rawness decreasing with increasing pulping chemical. The bursting and tensile strength, at 600 ml. S. R., increased with increasing chemical and were considerably greater than for the lime-cooked pulps. Tear resistance was practically unaffected but crush resistance increased with the greater use of sodium sulphite to a value well above that obtained by lime cooking. The pH of the waste liquors, ranging from 5.4 to 6.6,

also attests to the rawness of these pulps, previous work already having shown that sodium sulphite waste liquors with pH values below 6.0 indicate relatively brittle pulps.

Caustic soda. Coarse straw pulp has been produced with caustic soda for some time in Europe. The pulp is produced in lower yield than is usual in American practice, and chemical costs are considerably higher. The straw soda pulp, stronger than the usual lime-cooked product, is used in Europe for coarse wrapping and other papers as well as for corrugating.

With increasing amounts of caustic soda yields of the experimental pulp decreased fairly regularly and were lower than those obtained with lime or with sodium sulphite (Fig. 1). The pH values of the caustic waste liquors varied from 7.9 to 10.1. The soda pulps required less beating than the sodium sulphite pulps to reach 600 ml. freeness, and except for those pulps made with the larger amounts of caustic, they were harder than the lime-cooked pulps. Compared with the sodium sulphite pulps, the caustic pulps had better bursting strength and crush resistance, equal tensile strength, and lower tear resistance. The crush resistance of the soda pulps was considerably better than that of either the lime or the sulphite-cooked products.

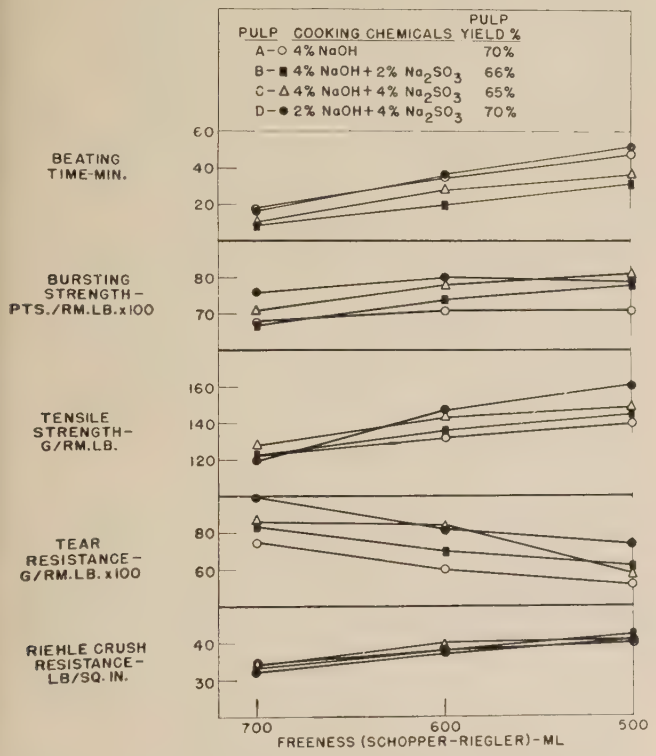
PULP COOKING CHEMICALS PULP YIELD %
A-○ 4% NaOH 70%
B-■ 4% NaOH + 2% Na_2SO_3 66%
C-△ 4% NaOH + 4% Na_2SO_3 65%
D-● 2% NaOH + 4% Na_2SO_3 70%
BEATING TIME-MIN.
BURSTING STRENGTH-PTS./RM.LB.x100
TENSILE STRENGTH-G/RM.LB.
TEAR RESISTANCE-G/RM.LB.x100
RIEHLE CRUSH RESISTANCE-LB/SQ. IN.
FREENESS (SCHOPPER-RIEGLER)-ML

Fig. 3. Effects of adding Na_2SO_3 to NaOH in cooking straw for corrugating

Combinations of Chemicals

Lime-caustic soda. The effects of adding 1.5 to 4% caustic soda to 6% lime for cooking straw are illustrated in Fig. 2. The yields of washed pulp remained practically constant except for a small reduction obtained with the largest amount of caustic used, 4%. All of the pulps were fairly soft, and to approximately the same degree as indicated by the time required to reach a freeness of 600 ml. The bursting and tensile strengths tended to increase and the tear resistance to decrease with increasing use of caustic soda. The regular, though small, decrease in crush resistance with increased amounts of caustic was not anticipated, however, because of the beneficial effects obtained in pulping straw with caustic alone (Fig. 1). It thus appears that the pulping characteristics of lime and of caustic soda on straw are not additive in their effect on the crush resistance of the resulting pulp, at least within the range of the amounts of chemical used here.

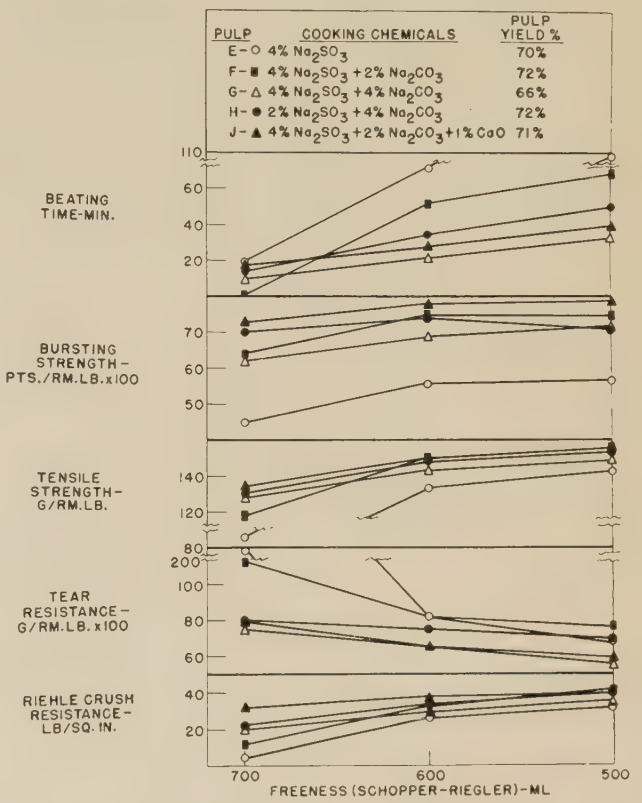
PULP COOKING CHEMICALS PULP YIELD %
E-○ 4% Na_2SO_3 70%
F-■ 4% Na_2SO_3 + 2% Na_2CO_3 72%
G-△ 4% Na_2SO_3 + 4% Na_2CO_3 66%
H-● 2% Na_2SO_3 + 4% Na_2CO_3 72%
J-▲ 4% Na_2SO_3 + 2% Na_2CO_3 + 1% CaO 71%
BEATING TIME-MIN.
BURSTING STRENGTH-PTS./RM.LB.x100
TENSILE STRENGTH-G/RM.LB.
TEAR RESISTANCE-G/RM.LB.x100
RIEHLE CRUSH RESISTANCE-LB/SQ. IN.
FREENESS (SCHOPPER-RIEGLER)-ML

Fig. 4. Effects of adding Na_2CO_3 to Na_2SO_3 in cooking straw for corrugating

The one outstanding characteristic of lime when used in combination with other chemicals in cooking straw for strawboard, is its effect in reducing the time and, consequently, the power required to beat or hydrate the resulting pulp. The higher pulp yields obtained in cooking with even moderate amounts of lime, owing in part to the retention of lime compounds, are counterbalanced to a large extent by the general inferiority of the strength properties and other characteristics of the pulps.

Caustic soda-sodium sulphite. A number of cooks were made with varying proportions of caustic soda and sodium sulphite. A portion of the data obtained is shown in Fig. 3. The yields of washed straw pulp decreased with the addition of up to 4% sulphite to the 4% caustic used for cooking. The yield of pulp from D (2% NaOH + 4% Na_2SO_3) was practically equal to that of A (4% NaOH), indicating that, in yield of washed strawboard pulp, 2% Na_2SO_3 is approximately

equivalent to 1% NaOH for cooking straw. This relationship was found valid for all caustic-sulphite combinations within the range of total chemical required to produce a satisfactory strawboard pulp. If this relationship will hold true in large-scale operation it can serve as a useful empirical tool in straw pulping control.

The freeness values of strawboard stock from the cylinder vats of a large number of paper machines were

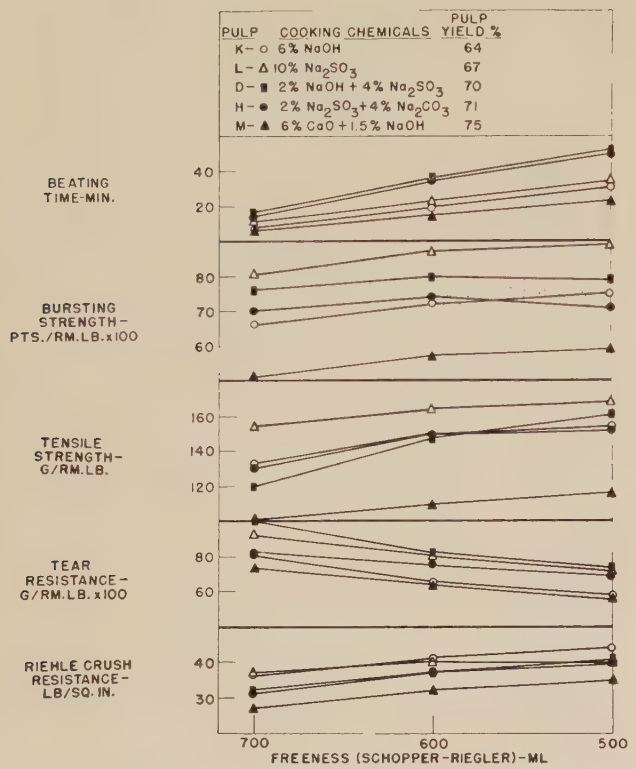

Fig. 5. Yields and properties of corrugating straw pulps produced with sodium compounds as compared with regular lime cooked pulp

found to be between about 600 and 700 ml. S. R. (280 to 400 ml., Canadian Standard) with the majority being close to 600 ml. It appeared logical, therefore, to use freeness of the pulp as a basis for comparison of the pulping effects of the various combinations of chemicals. The values shown in Figs. 3, 4, and 5 were taken from beater curves of the individual pulps.

The results in Fig. 3 show the increased time of beating, bursting and tensile strength and crush resistance, and the decrease in tear resistance as freeness was reduced from 700 to 500 ml. S. R. (400 to 210 ml. Canadian Standard). At a freeness of 600 ml. evaluation of the beating and strength characteristics of the pulps produced with the different combinations of chemicals shows that, in general, the best pulp was D, followed closely by C, B, and A, in order of decreasing strength values. It is apparent from a comparison of pulps C and D that the relative amounts of caustic and sulphite are as important as the total amount of chemical used for pulping the straw. The relatively small spreads between the strength values of the four pulps—9 points in bursting strength, 15 grams in tensile strength, 22 grams in tear resistance, and 2 pounds in Riehle crush resistance—indicate that the four combinations of chemicals may be equally suitable for producing good quality pulps for strawboard.

Sodium sulphite-sodium carbonate. The yields of straw pulps made with combinations of sodium sulphite and soda ash (Fig. 4) varied but little, except for pulp G which, produced with the largest total amount of chemical, had a somewhat lower yield. Cook J was included in this series because one strawboard mill had reported beneficial results from the addition of a small amount of lime to the neutral sulphite pulping liquor. Also previous work had shown that suitable strawboard pulps could be made with combinations of sulphite and lime (*3*).

The relative rawness of the pulps, or time required to beat to a definite freeness, decreased with increasing amounts of soda ash used for pulping. Pulp G, produced with the largest total amount of chemicals, was the softest. The addition of 1% lime to the sulphite-carbonate cooking liquor exerted a considerable softening effect on the resulting pulp, as illustrated by pulps F and J.

The straight sulphite pulp, E, was weaker in all properties, except tear resistance, than the pulps produced with mixtures of sulphite and carbonate. With sodium sulphite held constant an increase of soda ash in the cooking liquor from 2 to 4% of the weight of dry straw showed a tendency to decrease the strength properties of the resulting pulps, but the actual differences in these values were quite small. Pulps F and H, produced with the same total amounts of chemicals but with the proportions of sulphite and carbonate reversed, seemed to be of approximately equal strength. As usual, the rawest pulps had the highest tear resistance. Pulp J was the best of this series. It had the best bursting, tensile, and crush characteristics, thus corroborating on a pilot scale the results obtained in mill operation.

General Considerations

A comparison of the better pulps produced in this series of cooks is shown in Fig. 5. It is evident that the caustic-sulphite (D) and sulphite-carbonate (H) pulps were the hardest and the lime-caustic (M) pulp the softest. This is indicated by the time required to beat them to a definite freeness. Pulp M, typifying a relatively strong lime-cooked product, was definitely weaker in all respects than those produced with the sodium compounds. Pulp L, the straight sulphite product, at a freeness of 600 ml. S. R., was the strongest in all characteristics, followed closely by pulp D. Pulps K and H were fairly similar in strength properties except for the greater crush resistance of K, the straight caustic pulp. The caustic pulp was superior to all of the other pulps in the very important crush resistance.

Although insufficient data are available for determining the actual costs of producing strawboard pulps with chemicals employed in these studies, a comparison of the raw material and chemical costs provides some interesting information. The estimates given in the accompanying table show that the pulp costs decrease in the order: L, K, D, H, M. Thus, in general, the

strongest pulps cost the most to produce. The higher costs are not due solely to the chemicals involved; they are reflected also by the lower yields of pulp obtained.

Despite the higher costs, many strawboard mills are now using the sodium compounds discussed here for pulping straw for corrugating. As usual, each mill uses its own modifications of these chemical combinations depending largely on the pulping and refining equipment available and on the practices developed in the particular mill. The main reason for this change in pulping practice stems from the necessity to produce corrugating paper with superior strength properties, particularly crush resistance, and to reduce some of the operating difficulties encountered with the use of pulp cooked with lime alone or with appreciable amounts of lime. As indicated previously, the objective of adding a small amount of lime to the cooking liquor as in one mill and probably in others, too, has been to soften the pulp without materially reducing its strength properties.

Table I. Estimated Cost of Materials Per Ton Air-Dry Pulp

Pulp	*CaO,*[a] $	*NaOH,*[b] $	*Na_2SO_3,*[c] $	*Na_2CO_3,*[d] $	*Straw,*[e] $	*Total,* $
L	..	..	7.20	..	20.86	28.06
K	..	5.31	..	..	21.84	27.15
D	..	1.62	2.78	..	20.02	24.42
H	..	..	1.35	1.25	19.46	22.06
M	0.70	1.10	..	..	18.20	20.51

[a] $10.00/ton.
[b] $61.00/ton (solid).
[c] $50.00/ton (Anh. crst.).
[d] $25.00/ton (light).
[e] $14.00/ton.
Chemical prices as of November 1949, f.o.b. works.

The degree to which a pulp is beaten has a very decisive effect on the strength of paper obtained, as shown by the curves in Figs. 3, 4, and 5. Strength values of all the pulps increase with increased beating. For example, taking crush resistance as a criterion, the lime-caustic pulp, *M* (Fig. 5), beaten to a freeness of 500 ml. was superior to pulps D and H, beaten only to 700 ml. Thus the degree, and probably also the type, of refining given the straw pulp may be fully as important as the chemicals and methods used for pulping. If, as generally assumed, the stiffness of a paper is dependent on the amount and degree of hydration of the hemicelluloses present in the constituent pulps, straw pulps with their high hemicellulose content should be capable of producing excellent stiff products.

SUMMARY AND CONCLUSIONS

1. A large number of experimental straw pulps were prepared and tested, in collaboration with several strawboard mills, in an attempt to produce corrugating pulps with superior strength properties, particularly crush resistance.

2. Pulps prepared with caustic soda, sodium sulphite, and with combinations of these chemicals, were distinctly stronger than lime-cooked pulps.

3. The optimum results were obtained with 6% NaOH, 10% Na_2SO_3, 2% NaOH plus 4% Na_2SO_3, and 2% Na_2SO_3 plus 4% Na_2CO_3.

4. For providing good strength characteristics, suitable refining of straw pulp may be fully as important as the method of its preparation.

5. The high hemicellulose content of straw pulp provides a basis for producing corrugating paper with excellent crush resistance.

6. The results of this work offer the operating strawboard mills a wide latitude in choice of cooking chemical to produce the desired improved product consistent with the variation in methods and equipment used in each mill.

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Mechanism of the Retention of Beater Added Urea Resins

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Review of the literature on the application of urea-formaldehyde wet-strength resins to paper shows that controversies exist about both the mechanism of the process and the performance to be expected. Experiments described leave no doubt as to the importance of the ionic character of both resin and pulp to the mechanism of retention. There appears to be no reason to isolate the problems of urea resin retention from those of other beater additives such as rosin, dyes, fillers, and melamine resins. Cationic urea resins are found to give high efficiencies even on thoroughly bleached pulps. Statements about the performance of urea resins as a class are shown to be precarious, however, unless both resins and pulps are defined in detail.

The production of wet-strength paper is now one of the fastest growing applications for formaldehyde resins. Although understanding of the mechanism of the production of wet strength has by no means caught up with the art of the application, many thoughtful reports relating to the mechanism have been published.

Consideration of the action of wet-strength resins shows that three more or less separate problems are involved. The first is the intrinsic capacity of the resin to produce wet strength. The second is the

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retention of the resin in the sheet when, as is usual, the resin is added to the stock before the wire. The third is the curing or thermal treatment of the resin in the sheet which is required for realizing its wet-strength potential.

A description of experiments designed to examine the first question, the intrinsic capacity of resins to develop wet strength when applied to finished paper, has recently been given (*1*). In that report the chemistry of formaldehyde resins was discussed in a way which showed the wide range of properties which could be "built into" these resins by the methods of modern organic chemistry. The conclusion drawn was that, when adequately cured, wet-strength resins prepared from either melamine or urea gave papers having altogether comparable wet strengths.

The second question, the retention of the "beater added" resin in the finished sheet, has been dealt with more often. Studies of melamine resins (*3, 4, 5, 6*) are particularly noteworthy. These emphasize the importance of the positive charge (cationic character) and the relatively large size of the resin aggregates which are attracted by negatively charged (anionic) pulp colloids.

The literature shows that the mechanism of the retention of urea resins is a somewhat more controversial matter. This appears to be due, in part, to the many different kinds of urea resin which have been used. The versatility of the urea-formaldehyde system permits wide variation of ionic and hydrophilic character. Therefore, comparison of performance data obtained by investigators who do not report resin constitution is unjustified. The apparent contradictions in reports of different students of the retention of urea resins may, very likely, be due to real differences in the nature of the resins and pulps which were studied. The experiments to be described here have been aimed at a clarification of this situation. The opinion has been expressed (*12*) that the process of retention of urea resins is different than for melamine; and that a special kind of affinity might exist between the urea resin and the fiber, the nature of which is unknown. We have not found this difference. Our data show, essentially, the mechanism of retention of both urea and melamine resins is similar and is, principally, a function of the ionic character of the resin and of the pulp. Furthermore, for the first time, experiments with cationic urea resins are described which show the high efficiencies which are possible even on thoroughly bleached pulps.

A short review of the literature on the subject of the retention of urea resins serves to show the nature of the controversy which exists.

HISTORICAL DISCUSSION

The earliest published report on the retention of urea resins is that of Myers and Morin (*7*). These authors, using a commercial, bisulphite co-reacted urea-formaldehyde resin [Uformite 466 (now discontinued)] showed that useful results could be obtained with "beater added" urea formaldehyde resins. Their work showed clearly the importance of the "mordanting" effect of alum to the retention of this anionic resin which strongly suggested that here, as in the application of melamine resins, the ionic character of resin and ion exchange capacity of pulp were significant.

A later report by Bursztyn (*8*) confirmed the work of Myers and Morin and showed that even more efficient retention of the resin was possible. Under favorable conditions he found more than 90% of the beater applied urea resin in the sheet.

Subsequent studies (*9, 10, 11, 12, 13, 14*) made extensions on the earlier works. With the exception of Henrikson and Steenberg (*12*) however, none of these investigators made any effort to characterize the urea resins which were studied. The work of Schofield and Harrison (*10*) is noteworthy for the systematic study of the effect of pulp bleaching on urea resin retention. They found that their urea resin was not substantive to true cellulose, but to one or more of the compounds associated with unbleached fiber.

Bursztyn's later work (*13*) concerns the poor retention of his urea resin preparation on a bleached pulp. He does point out, however, that in England 30 tons of wet-strength paper are made with urea resin to each ton made with melamine resin.

Because of their discussion of the preparation and characterization of the urea resins which they used, the paper by Henrikson and Steenberg (*12*) has particular importance. Although they by no means exhaust the range of variation which is possible, 100 specially prepared resins were examined. Ionic character of the resin (controlled by addition of co-reactant) and degrees of condensation (controlled by viscosity) were systematically varied. When the degree of condensation was sufficiently high all of the resins were found to show uniformly good efficiencies in producing wet strength without regard to ionic character.

In view of earlier studies which had suggested that the ionic character of the pulp and resin should be of great importance, Henrikson and Steenberg were unable to explain the results of this experiment.

The work described and the discussion given in the present paper indicate that the indifference of resin performance to ionic character observed by Henrikson and Steenberg may have been due to peculiarities of the pulps which were used in their experiments. On the other hand, the possibility that differences in application conditions or in the nature of the resins used were responsible, cannot legitimately be excluded.

It has long been known that some pulps are more difficult to size and have lower affinity for rosin than others. Schofield and Harrison (*10*) show that affinity for some urea resins also varies from pulp to pulp and, just as with rosin, the more highly bleached pulps had the lower affinities for their resins. A paper by Sigvardt (*15*), which concerns the dyeing of various pulps with cationic dyestuffs, provides a rationalization for these observations in terms of the number and character of the ionic groups in the fiber. Gruntfest (*16*) later applied the conclusions of Sigvardt to the problem of resin retention.

It appears in the experiments to be described that the sulphite and sulphate pulps used by Henrikson and Steenberg may have had such strong affinities for resin that saturation effects were obtained with many resin preparations which might have differed greatly from one another if a more sensitive index of their char-

acter had been used. The present work, however, gives only slight support to that possibility.

EXPERIMENTAL

The data presented below have been selected to show how variations in the character of the "beater added" urea resin influence its retention in the finished sheet. Pulp and alum variation are also considered. Performance figures for a melamine wet-strength resin are included for comparison. These results are entirely compatible with modern theories of the retention of rosin size, dyestuffs, and fillers. In fact they provide further support for these theories. Furthermore, in the light of the experiments, it is possible to give some explanation for the results which surprised Henrikson and Steenberg (*12*).

The anionic and cationic urea resins used in the present work were highly condensed, modern commercial products (Uformite 467 and Uformite 470, respectively) designed as beater additives for the production of wet-strength paper. The nonionic urea resin was a highly condensed commercial product (Uformite 414) which has been used to prepare wet-strength paper by tub sizing. The essential differences among these resins is the presence or absence of small amounts of co-reactant of appropriate ionic character.

The melamine resin was also a commercial product (Parez 607) prepared according to the specifications of the supplier.

The paper used for tub sizing was a water-leaf bleached sulphite of 35-pound basis weight 25 × 40—500). "Beater added" data were obtained on handsheets made on an 8 by 8 inch Valley mold according to TAPPI Standard methods except as indicated. The basis weight of the handsheets was held at 35 pounds. Pulps were lightly beaten to Canadian freeness of 500 to 600 ml. Resins were added in the disintegrator and alum addition and pH adjustment were made at this point. The pH of the dilution water was also adjusted.

The treated paper samples were held in an oven at 150° C. for 15 minutes which largely eliminated the necessity for catalyst and assured full cure. Less heat was required for melamine treated papers.

Strengths are reported as pounds per inch of width. Wet strengths were taken after 1 hour of soaking in pure water held at 70° F.

TUB SIZING

Three per cent solutions of all four resins were applied to the bleached sulphite saturating paper to a pickup of about 120%. In order to simplify the problem of defining the exact state of cure, maximum strength values are reported. This makes the data here comparable with that given by others (*12*).

Table I. Effect of Resins Applied by Tub Sizing

Resin (3.6% added)	*Dry strength*	*Wet strength*
No resin	4.6	0.8
Nonionic	9.0	4.8
Anionic	9.8	5.7
Cationic	10.4	5.9
Melamine	10.3	5.8

The data in Table I show that the intrinsic capacity of all four resins to develop wet strength when applied to finished paper is very similar. This would have been expected on the basis of earlier work (*1*). It is emphasized here because maximum strength developed is the only criterion for resin performance used in the experiments described here. While maximum wet tensile is not an ideal index of resin retention it is adequate for the gross differences in performance which are shown here.

BLEACHED SULPHITE WITHOUT ALUM

The results of the first beater added experiments shown in Table II stand in strong contrast to the figures in Table I. The four resins which show similar performance in the tub are very different when applied, in the beater, without alum, to bleached sulphite pulp. The implication is that only cationic resins are retained in the sheet under the conditions of the experiment.

Although the comparison of the urea and melamine resins is instructive, the figures do not represent the usual results obtained in a mill. There the melamine resin, which is faster curing, comes closer to ultimate strength in the drier section of the paper machine.

Table II. Effect of Beater Added Resins on Highly Bleached Sulphite without Alum[a]

Resin 3% on pulp	*Dry strength*	*Wet strength*
No resin	5.4	1.2
Nonionic	6.5	1.7
Anionic	6.8	1.7
Cationic	10.0	5.3
Melamine	9.4	4.1

[a] The pH of the mixture in the disintegrator and of the dilution water was adjusted with HCl to 4 for this experiment.

This outcome shown in Table II is entirely compatible with the current ideas of the anionic character of pulp colloids.

UNBLEACHED KRAFT WITH ALUM

Although the anionic character of the pulp colloids requires the use of a cationic resin for direct application in the beater, anionic resins have a large range of usefulness as is shown by the data in Table III. Here alum is used to mordant the anionic resin to the anionic pulp. Apparently, here, the cationic alum has not seriously interfered with the retention of the cationic resins.

In this experiment the pH of the mixture in the disintegrator and of the dilution water was adjusted to 4. Three per cent of alum on dry pulp was added with the resins in the disintegrator.

Table III. Effect of Beater Added Resins on Unbleached Kraft with Alum

Resin 3% on dry pulp	*Dry strength*	*Wet strength*
No resin	10.2	1.2
Nonionic	15.0	3.4
Anionic	20.5	8.2
Cationic	21.0	9.1
Melamine	19.4	6.6

These data (Tables II and III) show conclusively

that completely different results can be obtained with different urea resins. Hence generalizations about the efficiency or inefficiency of urea resins as a class are totally invalid unless the characteristics of the particular resin under consideration are first carefully defined.

BLEACHED SULPHITE WITH ALUM

The mordanting action of alum is also shown, though less strikingly, by experiments with bleached sulphite. Here again the performance of the anionic resin is improved by the addition of alum and that of the cationic resin is unimpaired. Conditions of this experiment are identical with that using unbleached kraft (Table III).

Table IV. Effect of Beater Added Resins on Highly Bleached Sulphite with Alum

Resin 3% on pulp	*Dry strength*	*Wet strength*
No resin	5.5	1.2
Nonionic	8.3	2.4
Anionic	9.0	3.3
Cationic	10.0	5.3
Melamine	10.0	4.4

UNBLEACHED KRAFT WITHOUT ALUM

The indifference of resin performance to the ionic character of the resin, reported by Henrikson and Steenberg (*12*), has never been observed in this laboratory. However, some indication that such results might be possible with selected pulps of high affinity is given by the data in Table V.

Table V. Effect of Beater Added Resins on Unbleached Kraft without Alum

Resin 3% on pulp	*Dry strength*	*Wet strength*
No resin	11.0	1.2
Nonionic	15.5	3.5
Anionic	15.8	3.6
Cationic	21.4	7.5
Melamine	18.6	5.5

The conditions of this experiment were identical with those applied to bleached sulphite (Table II). Notice in Table V that the failure of the anionic resins, used without alum, is somewhat less conspicuous than was shown in Table II. This result indicates that factors other than the ionic character of the resin may be operative, especially when unbleached pulps are used.

DISCUSSION

Examination of experiments described above seems to leave no doubt about the relevance of the ionic character of the resins to their performance. Furthermore, it appears that the modern theories (*15*, *16*) of the colloidal nature of pulps, which were developed in connection with the application of rosin size, dyes, and fillers, also pertain to the retention of urea and melamine resins. This conclusion is especially important since earlier investigators (*12*, *14*) have argued that the retention of urea resins is essentially different from other retention problems.

The lack of resin specificity shown in experiments with unbleached pulps by Henrikson and Steenberg (*12*) may reside in the attraction between the resin nitrogens and the surface of the pulp colloid. Such an attraction could be due to the mild cationic nature, or salt forming capacity, of these nitrogens. On the other hand, the strong tendency for hydrogen bonds to form between the cellulose oxygens and the resin nitrogens might be a more significant source of the attraction. Both of these suggestions are purely speculative and there appears to be no basis for making a choice.

However, the importance of the nonspecific attractions between resin and pulp is not shown very forcefully in the present experiments. It is somewhat unfortunate, in connection with the definition of these attractions, that alum was used indiscriminately in all but one of the experiments described by Henrikson and Steenberg. This reduces the usefulness of their experiments and the validity of their conclusion.

There is also no way to know precisely what the differences might be between the resins used by Henrikson and Steenberg and those used in this work. The fact that the extremely interesting dependence of resin performance on degree of condensation (i.e., viscosity) which they observed is very similar to results obtained in this laboratory indicates that there were some similarities among the resins. On the other hand, while their urea resins were comparable with melamine in producing wet strengths after ultimate cure, the resins used here were generally superior. Furthermore, it is known that the co-reactants used to produce the cationic resins described in the earlier paper were different from those in the resins used here. Also, no information is given in connection with the extremely important factor, the amount of co-reactant.

In conclusion, while the question of the mechanism of the retention of urea resins deserves further study, there appears to be no cause for isolating this particular retention problem from others which concern paper technologists.

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Factors in White Water Treatment

V. J. CALISE

This paper deals with various types of equipment now available for reducing loss of stock in white waters from pulp and paper mills. In particular, two modern designs of reclaimers are described in detail, both embodying the principle of contacting the incoming white water with previously accumulated solid precipitates and stock in order to effect virtually complete removal stock from the white water. An actual example of a complete engineering calculation of such a reclaimer installation is shown with equipment costs, installation costs, operating costs, and savings obtained.

WATER is the major raw material employed by most industries and utilities. Consequently, two important problems are presented in manufacturing and utility operations: (1) obtaining a low cost, abundant supply of water which is satisfactory for various plant requirements; and (2) disposing of contaminated or polluted waste waters after use.

The usual methods of water treatment such as coagulation, flocculation, and sedimentation, lime-soda or zeolite softening and filtration have been successfully employed in making all kinds of raw water supplies useful for plant operations.

It is the purpose of this paper to discuss some of the economic factors entering into the selection and operation of white water treatment installations in pulp and paper industries.

In some plants, proper treatment of white waters can help solve the problem of insufficient or high cost raw water by providing a supply of clarified water of proper chemical composition. This is of special value where normal surface supplies are insufficient during most of the year or where they are highly polluted and costly to purify, and also where the underground water table is very low and water is costly to obtain in adequate quantities.

In many cases, the recovery of costly stock from the white water results in savings of many thousands of dollars per year in addition to solving the waste disposal problem.

RESTRICTION ON DISPOSAL OF WASTE WATERS

Most states have adopted rigid regulations prohibiting the introduction of wastes into rivers and streams.

The seriousness of the problem of stream pollution by waste waters containing large quantities of pulp and paper stock, mainly cellulosic in nature, is apparent to all pulp and paper-mill owners. A great deal of work is being done by this industry and various trade groups so as to conform to regulations of state sanitation boards. In contrast to many industries where usable materials cannot be recovered from wastes, the treatment of white waters can be profitable by recovering pulp and paper stock. State regulations now require reduction of solids in pulp and paper-mill waste waters to values low enough to avoid increasing the pollution load on streams and surface supplies. In many cases this means a permissible suspended solids or stock concentration of less than 0.25 pound per thousand gallons in the waste water discharged into the stream.

More and more states, cities, and towns are establishing regulations limiting impurities which can be tolerated in open streams and local sewerage systems. The assistance of the Federal government is now available to help solve problems presented by the waste waters of industry.

FACTORS IN DESIGN AND COST OF WASTE WATER TREATMENT EQUIPMENT

There are many waste water problems of such complexity and diversity that laboratory research and pilot plant developmental investigations are required before the chemistry of the treatment process and the equipment design are established. However, there are also a number of problems and applications where the pattern of waste water composition, chemical treatment, and equipment design are well established on the basis of experience and operating data with existing installations.

The selection of the proper process and equipment for treating any waste water are mainly a problem in economics. It is the job of the equipment engineer to select the process and chemical dosages and design the equipment which will yield the required purity of treated waste water at lowest cost and with greatest convenience in fitting into the existing plant flow sheet.

Aside from the requirements of foolproof design and proper performance results, it is usually important to reduce the long-term operating cost of waste water treatment plants to the very lowest values. The factors which enter into the long-term operating costs are: (1) cost of chemicals required for treatment, (2) initial investment required for installed equipment, (3) maintenance of equipment parts, (4) cost of labor for operation of equipment, and (5) possibility of recovering valuable products or reusable water from waste water.

The application of chemical and mechanical skill, combining up-to-date developments and experience with on-the-spot investigational research data will appreciably reduce long-term operating cost and provide an installation best fitted to the specific plant conditions.

TREATMENT OF WHITE WATERS FROM PULP AND PAPER MILLS

The amount of stock comprising both fiber and filler which is discharged and lost in waste waters from pulp and paper mills can be quite high. In Table I the concentrations of stock in white and waste waters from four mills are shown. In some large paper mills

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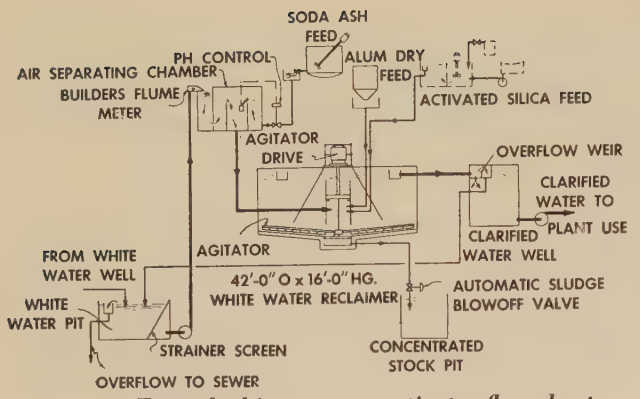

Fig. 1. Typical white water reactivator flow sheet

as much as 6 tons and as high as 50 tons of stock, on a dry basis, are lost per day.

Table I. Stock Concentrations in White Water

Mill	*Amount of white water discharged, g.p.m.*	*Range of solids concentration, lb./M gal.*	*Amount of stock (fiber and filler) lost, lb./hr.*	*Range of pH of white water*
A	400	3– 4.5	90	5.5–6.5
B	1400	4–12	500	3.8–5.5
C	2000	2–4	360	5.5–7.0
D	1200	3–6	290	4–7

The reason for this loss lies in the inability of the fourdrinier wire or any wire used in savealls or other machines to effect a complete separation of suspended solids in water.

There are a number of devices for treating white and waste waters from paper mills. These savealls can be classified by the methods employed in separating fibers and fillers from the water as follows:

1. Screen filtration without pretreatment.
2. Settling in large retention basins with or without chemical pretreatment.
3. Pretreatment with chemicals and pressure aeration followed by flocculation and skimming.
4. Coagulation with chemicals and clarification in a solids contact reclaimer.

It is the purpose of this paper to discuss design, performance, and operating costs obtained with solids-contact reclaimers under item 4 above.

With the savealls listed under items 1 to 3 above, the separation of the fibrous solids is accomplished mechanically, either by retaining the fiber on a fine mesh wire screen or by using large tanks so that the velocity of flow is so small that the fibers settle by gravity to the bottom, or by adding reagents which float the fibers to the top. With these devices, once the fiber or stock is separated, it is withdrawn from the scene of action and no longer plays any part in the treatment of the waste water.

Although the quality of effluent obtained with these savealls may be satisfactory for some reuse applications, it may not be satisfactory for many cases, particularly where the clarified waste water is employed for showers. For many such applications, concentrations of stock of less than 0.25 pound per thousand gallons are required in the clarified waste water. Such low concentrations are easily obtained in solids-contact reclaimers.

SOLIDS-CONTACT RECLAIMERS

Solids-contact reclaimers make use of a principle which has been employed successfully for many years in the chemical treatment of water supplies. The principle of operation is to provide prolonged contact of the incoming waste water and chemicals with a large concentration of previously accumulated suspended solids. Intimate contact with the suspended solids provides vast adsorptive surface areas to which the coagulated stock particles can adhere providing more effective and more complete coagulation while increasing the average size and weight of the stock particles which settle out more rapidly. The result of providing proper contact with solids is the removal of more than 95% of incoming waste water solids in a minimum of time and space.

Figure 1 shows a diagramatic sketch of a reactivator-type solids-contact reclaimer and a flow sheet illustrating a typical plant installation. As shown in Fig. 2 an agitator pump is provided in the central uptake of the unit, which mixes water, chemicals, and recirculated solids. Accumulated solids are recirculated by means of this agitator pump at two to six times the rate of flow of influent to and effluent from the reclaimer. The mixture of water, chemicals, and solids leaves the uptake and enters a conical flocculation zone where particles are permitted to coalesce and chemical reactions are further completed. At the bottom of the conical section the mixture is made to flow upwardly to the collector through a settling section of increasing upward area and, therefore, continuously decreasing vertical velocity. The heavy, large particles are permitted to settle out on the large bottom area and are continuously moved toward a center sludge pit by means of slowly rotating sludge scraper blades. Lighter solids separate from the effluent water stream at the bottom of the conical section and are recirculated up through the central uptake by the agitator pump.

The main features of a solids-contact reclaimer of this type are:

1. Intimate and prolonged contact of solids with the mixture of water and chemicals is provided and can be easily varied.
2. Positive and independent recirculation of previously formed solids by means of the agitator pump is provided. This minimizes the effects on effluent quality of sudden wide fluctuations in flow rate through the unit.
3. Positive movement of settled solids to a concentrated sludge pit is provided by means of rotating scraper blades. This avoids the problem of depending on plant flow rate and vertical hydraulic flow for lifting solids to elevated concentrator pockets. Also, it assures positive removal of all accumulated solids at all times.
4. The very large settling area (virtually the full bottom) of the unit is available for accumulating settled solids. This avoids the problem of location and inadequate size which occurs in circumferential elevated sludge concentrators.

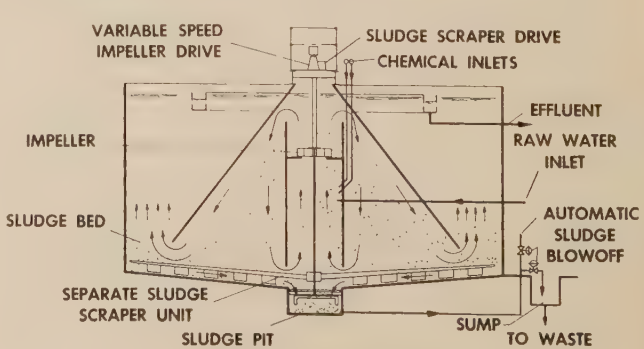

Fig. 2. Graver reactivator (solids-contact unit)

Coagulating chemicals, where necessary, are fed by a proportionating pump or a wet-type proportionating feed. The wet-type proportionating feeder consists of an inclined drawoff pipe, the top head of which is suspended by a chain wound around the feeding sprocket of the chemical feeding device. A totally enclosed, motor-operated gear reduction unit of special design causes the sprocket to rotate. During operation of the feed, the chemical tank is filled with the chemical solution or suspension and the feeding sprocket rotates, slowly lowering the chain and the end of the drawoff pipe below the liquid level thus feeding chemical solution down the swing pipe at an accurate rate. An inlet flowmeter is usually employed to actuate the device through a contactor and timer arrangement. Feeding rates can be quickly and easily adjusted by remote control.

Although treatment chemicals are required in many cases there are applications where sufficient alum and other coagulants and coagulant aids are present in the waste water itself in sufficient quantities to avoid requiring additional chemicals. This somewhat simplifies plant operation and reduces operating cost slightly.

Economics of Treatment

As an example of over-all cost for treatment of white water by solids-contact reclaimers, let us consider a paper mill where the following conditions are found:

Maximum amount of white water discharged to waste	2,000,000 g.p.d.
Average amount of stock in white water	2.5 lb./M gal.
Average temperature of wasted white water	85°F. Summer 70°F. Winter
Maximum amount of treated well water required	2,000,000 g.p.d.
Actual cost of treated well water	2¢/M gal.
Average temperature of well water	55°F.
Value of stock in white water, average	$35/ton

It is desired to install a solids-contact reclaimer to clarify the white water so that most of this treated water can be reused in the plant while most of the recovered stock can be recovered. Figure 1 shows a suggested flow sheet for this installation. The treated effluent from the saveall is to contain 0.25 pound per thousand gallons of stock.

Recovered Products

The stock recovered from this plant is: 2.5 − 0.25 = 2.25 lb./M gal., or $\frac{(2{,}000{,}000)\ (2.25)}{1000}$ = 4500 lb./day or 2.25 tons/day.

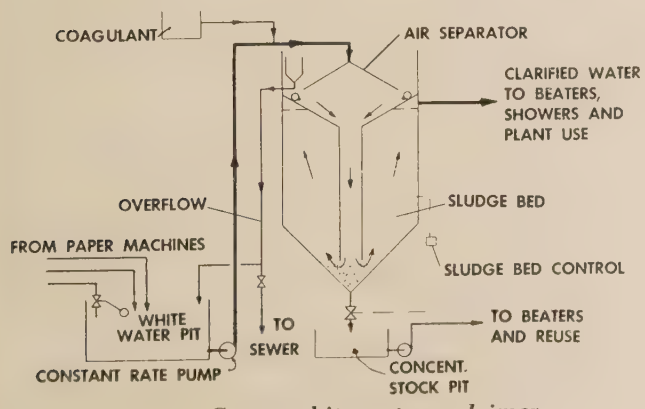

Fig. 3. Graver white water reclaimer

With the stock concentrated to 3% in the sludge pit then $\frac{4500}{0.03}$ = 150,000 lb. or 20,000 gal.

Recovered Water

Recovered waste water: 2,000,000 − 20,000 = 1,980,000 gal. Blowdown of treated white water discharged to waste to maintain total dissolved solids in recirculated water below 2500 p.p.m. = 25% or 400,000 g.p.d. Recovered clarifier white water for reuse: 1,980,000 − 400,000 = 1,580,000 g.p.d.

Recovered B.T.U.

1,580,000 g.p.d. recovered water; average recovered B.t.u. = $\frac{(85 + 70)}{2}$ − 55 = 22.50: (22.5°F.) $\frac{(1\ \text{B.t.u.})}{(\text{pound})\ (°\text{F.})}$ = 22.5 B.t.u. or (1,580,000) (8.3) (22.5) = 300,000,000 B.t.u./day.

Cost of Equipment

1400-g.p.m. unit as per Fig. 1; dimension − 40 ft. diameter by 15 ft. straight; $^5/_{16}$-in. steel shell on concrete pad bottom; complete with internal uptake, conical section controls, and accessories including: wet alkali proportionating feed with pH control, alum dry feed, activated silica feed, air separation tank, and concentrated stock automatic blowoff equipment,

approximate equipment cost	$45,000
Approximate cost of erection and installation, including foundations, etc., not including building or housing	$35,000
Approximate total cost	$80,000
Amortized equipment cost (10 years)	$ 8,000/year

Chemical Operating Cost

Soda ash = 0.3 lb./M gal. or 600 lb./day at 1.6 cents/lb. = $10/day or $3000/year	$ 3,000
Alum = 400 lb./day or $3.50/day or $1000/year	$ 1,000
Cost of labor per year	$ 8,000/year
Total costs per year	$20,000

Savings Per Year Due to Installation

Recovered stock − 2.25 tons/day − 50% used or 1.13 tons/day, valued at $35/ton = $39/day = $11,700/year.

Recovered water − 1,580,000 gal. at 2 cents/M gal. = $32.00/day or = $9,600/year.

Recovered heat − 300,000,000 B.t.u./day at average cost 20 cents/1,000,000 B.t.u. = $60/day or $18,000/year.

Total value of recovered products, $39,300/year and costs 20,000/year. Savings per year, $19,300.

These calculations indicate that the savings obtained under these particular plant conditions would permit payment of initial investment in about 4 years and thenceforth would permit savings of approximately $19,300 per year under stated price conditions. In addition, the problem of pollution of surface supplies is eliminated. Any concentrated stock not reused in the plant can be burned to avoid lagooning. Treated waste water can be discharged to waste without danger of pollution because it contains less than 0.25 pound per thousand gallons of stock.

A 100 g.p.m. solids-contact saveall unit of similar design would cost approximately $22,000 installed. The cost of machines for intermediate flows would be roughly proportional to values given above.

SIMPLIFIED SOLIDS-CONTACT RECLAIMER

Figure 3 shows a cross sectional sketch and flow diagram of a simplified Graver solids-contact reclaimer which can be employed for smaller plants where the nature of the solids is such that agitation, recirculation of solids, and positive sludge scraper solids removal are not necessary.

As shown in Fig. 3, there are no internal moving

parts in this machine. Incoming white or waste water merely flow over an air-separator baffle and mix with chemical, if required, in a long, high velocity downtake. The bottom edge of the downtake is designed so that it projects part of the way into the bottom cone. Accumulated solids are suspended by the upflowing water to provide a deep bed of sludge through which waste water and chemicals must pass to flow to the outlet collector. Very low upward settling velocities are employed, surrounding the downtake in this unit and this, together with the lower viscosity of warm water, assures maximum settling of coagulated solids. The bed of sludge is maintained at a low point in the unit and a very deep section of widest area is provided above the sludge bed to obtain optimum results. Accumulated solids settle down into the bottom of the cone and are automatically blown off to waste.

The equipment and installation costs for this simplified machine are considerably less than those for the solids contact unit shown in Fig. 2. The simplified reclaimer is very easy to install, can be located in the open without housing in moderate climate, and can be easily lagged to reduce heat losses. Chemical costs, where chemicals are required, are about the same as previously indicated.

With solids contact reclaimers of the types shown in Figs. 2 and 3, cost of chemicals for operation are usually very low. In many white waters sufficient alum or other coagulating material is present to avoid addition of more coagulant. In such cases, small quantities of alkali are usually fed to provide the optimum pH for coagulation as determined in laboratory or pilot plant tests. Lime or soda ash are usually employed for this purpose.

In other cases, a coagulant, alkali, and coagulant aid, such as activated silica, must be added to obtain proper floc density.

In most cases, such cost for chemicals averages less than 1 to 2 cents per thousand gallons of water treated.

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Production of High-Yield Pulps from Aspen by Mild Treatments with Sodium Hydroxide

K. J. BROWN and J. N. McGOVERN

In experiments at the U. S. Forest Products Laboratory, aspen (*Populus tremuloides*) chips were given mild treatments with sodium hydroxide solutions at atmospheric pressure and then mechanically fiberized to produce pulps in the yield range of 82 to 95%. Treatments were made with caustic solutions in concentrations of 24 and 63 grams per liter. Treating time varied from 15 minutes to 5 hours and temperature from 25 to 90°C. The optimum treating condition from the standpoints of the treating variables, pulp yield, and pulp strength was a 2-hour treatment at 25°C. with a sodium hydroxide solution having a concentration of 24 grams per liter. Chemical consumption for this treatment was about 5.5% sodium hydroxide, based on the weight of the wood, and a pulp yield of about 91%. Pulp made under these conditions was converted into corrugating board that compared favorably with commercial hardwood semichemical corrugating board in strength properties. The effects of the individual treatment variables are discussed.

High-Yield pulping has been receiving increasing attention in recent years in the endeavor to produce pulps in yields near those of groundwood pulps but with improved properties and wider uses. Its objective is closely tied in with those of wood conservation and the utilization of wood wastes and little-used species. The purpose of the work reported here was to obtain information on high-yield pulping in the range of pulp yields of 85 to 95%. This range is higher than that usually understood for semichemical pulping, and also differs basically from the latter in that partial delignification is preferably avoided. The present report is a continuation of work reported recently on steam and water cooking of wood chips (*2*). It gives the results of a systematic investigation of certain treatment variables involved in the experimental production of high-yield pulps from quaking aspen by a process consisting of a mild treatment of the chips with caustic soda, followed by their mechanical fiberization.

Although sodium hydroxide is the oldest of the commercial pulping agents, investigations reported in the literature on its use have mostly referred to the process of soda pulping, in which conditions are designed for a substantially complete removal of the lignin from the wood. In one study of the use of sodium hydroxide as a semichemical pulping agent, however, it was found that the pulps were much weaker than those made with sulphate pulping liquor (*1*).

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EXPERIMENTAL WORK

Peeled air-dry quaking aspen was used in these experiments. The wood was made into standard $^5/_8$-inch chips for pulping. The chips had a moisture content of approximately 10%.

Except for one experiment, the caustic soda treatments were conducted in a 0.5-cubic foot, steam-jacketed, tumbling autoclave. One treatment was made in a 13-cubic foot, stainless-steel-lined, tumbling digester. After treatment in the autoclave, the chips were fiberized in an 8-inch diameter, single-rotating-disk attrition mill. The treated chips obtained in

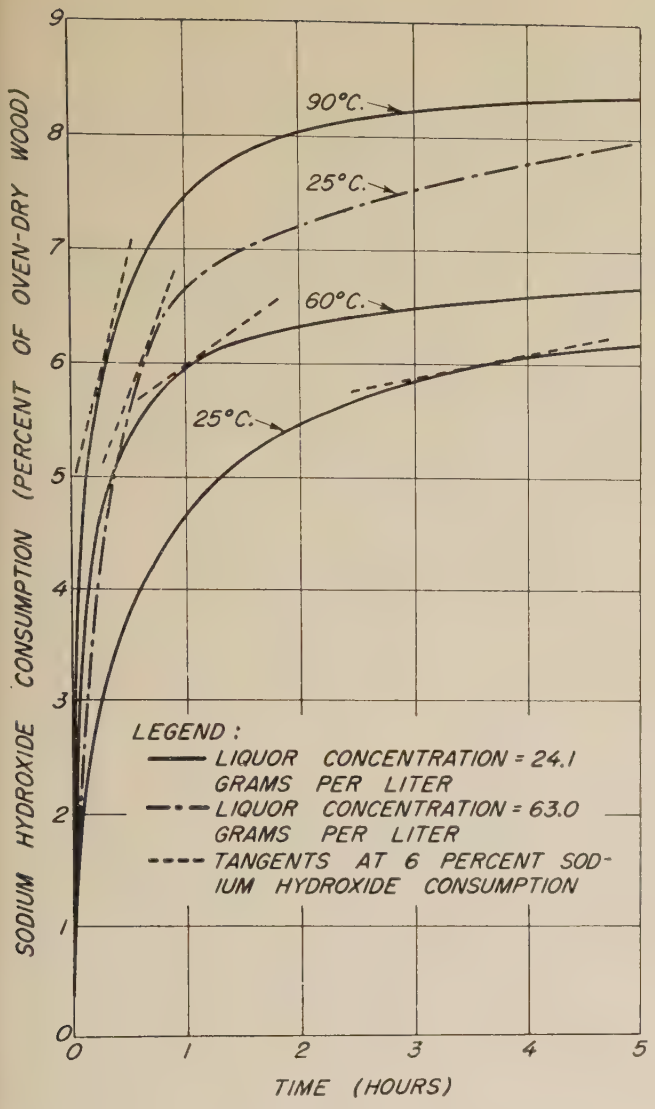

Fig. 1. Effect of time and temperature on sodium hydroxide consumption in the pulping of aspen chips

larger-scale experiments were fiberized in a 36-inch double-rotating-disk attrition mill. This pulp was converted into corrugating board on the Laboratory's 12-inch fourdrinier paper machine.

The digestions were conducted with a liquor-to-wood ratio of 5 to 1. For those experiments made at higher than room temperature, the liquor was heated to the treating temperature in the autoclave before the chips were added, thus eliminating the usual period of temperature rise with chips present. The treated chips were fiberized immediately after the caustic treatment after washing. The pulp yields were determined on the basis of the fiberized pulps. The pulps were beaten for strength development in a Valley beater by TAPPI standard methods and the 115-pound (weight per ream of 500 sheets, each 25 by 40 inches) test sheets made from the pulps were tested for strength by the standard methods. The pulps were also analyzed for their content of lignin, holocellulose, and alpha-cellulose by standard methods.

In one experiment, the $^5/_8$-inch chips were partially disintegrated before being given the caustic soda treatment, by passing them through the 8-inch attrition mill equipped with coarse breaker plates. This action broke down the chips mainly in the lengthwise direction and reduced them mostly to pieces having a maximum dimension of $^1/_8$ inch in the longitudinal and radial directions. There was present, however, a small percentage of fragmented material and small pieces less than $^5/_8$ inch in the grain direction. The disintegrated chips with a moisture content of 50% were then treated with a sodium hydroxide solution of 22.3 grams per liter concentration, and with a liquor-to-wood ratio of 6.3 to 1, for 2 hours at 25°C. The treated material was fiberized and handled as described above.

DISCUSSION OF RESULTS

Effect of Treatment Variables

The three independent treatment variables, time, temperature, and alkali concentration, had considerable effect on the chemical consumed, the yield of pulp, and the strength properties and chemical composition of the pulps.

Chemical Consumption

The effects of the treatment variables on sodium hydroxide consumption are shown in Fig. 1. Chemical consumption increased with increases in time, temperature, and alkali concentration. The rate of chemical consumption was very rapid at the start of the treatment; 50% or more of the total consumption in the 5-hour treating period was obtained in the first 15 minutes of that period. The rate was, however, very slow toward the end of the treating period. The lowered rate probably means that most of the hemicelluloses, which were readily soluble under the par-

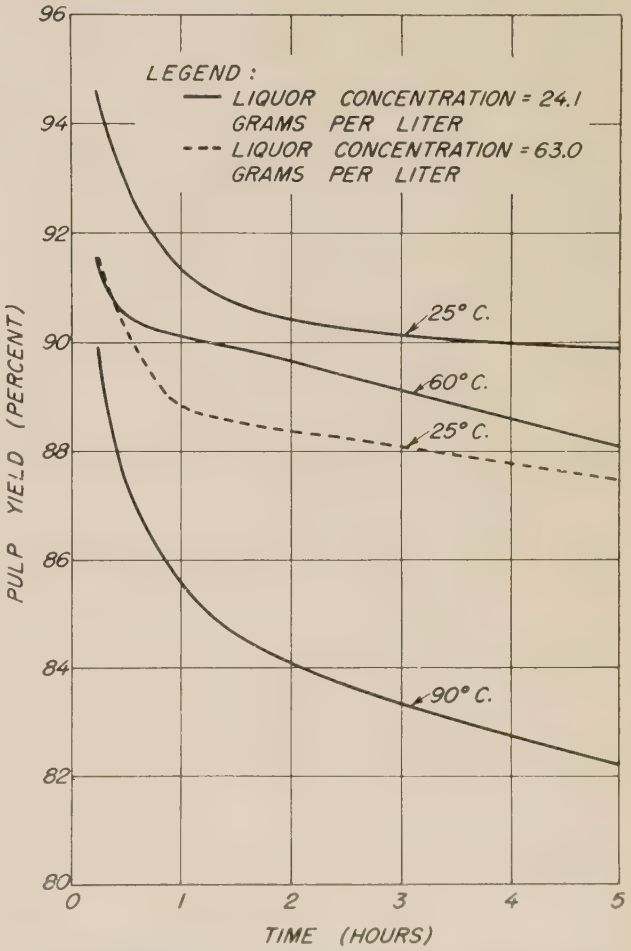

Fig. 2. Effect of time and temperature on yield of pulp from aspen treated with sodium hydroxide

ticular conditions of treatment, had by this time been removed from the wood.

The rate of chemical consumption increased with temperature at any given chemical consumption within the range of the experiments. This is obvious from the slope of tangents drawn on the consumption curves in Fig. 1 at a constant chemical consumption. By application of the Arrhenius law, the rate was found to be increased by approximately 175% for a temperature increase of 10°C.

The initial chemical consumption and the rate of consumption also increased with the stronger treating solution, as shown in Fig. 1.

Pulp Yield

The effects of the treatment variables on pulp yield are shown in Fig. 2. The rate of pulping, as measured in terms of reduction in pulp yield, was rapid during the first stages of the treatment and became very slow toward the end of the treatment. This again may have meant that the readily soluble material had been removed in the early stages of the treatments. The trend of the yield curves with respect to treating conditions paralleled that of chemical consumption with relation to treating conditions shown in Fig. 1. The relation between pulp yield and chemical consumption shown by Fig. 3 departed a little from a linear trend and indicated a chemical consumption which, for a given reduction in yield, was higher in the range above about 88% yield than in the range below that yield. This relation was independent of temperature and chemical concentration. A similar close relationship between pulp yield and chemical consumption in conventional soda pulping has also been reported (*3*).

Chemical Composition of the Pulps

The effect of the alkali treatment, as measured by the sodium hydroxide consumption, on the main chemical composition of the pulps is shown in Fig. 4. Neither the lignin nor the alpha-cellulose content of the pulps, apparently, was affected by the treatments within the range of the experiments. The holocellulose content of the pulps, on the other hand, decreased

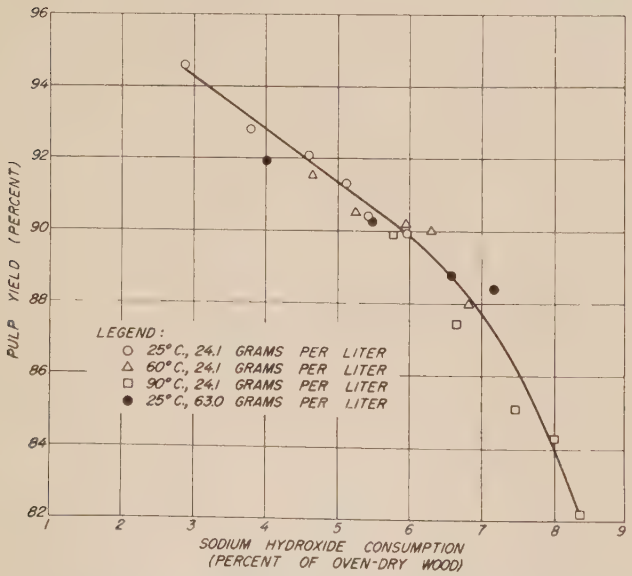

Fig. 3. Relation between yield of pulp from aspen and consumption of sodium hydroxide under several treating conditions

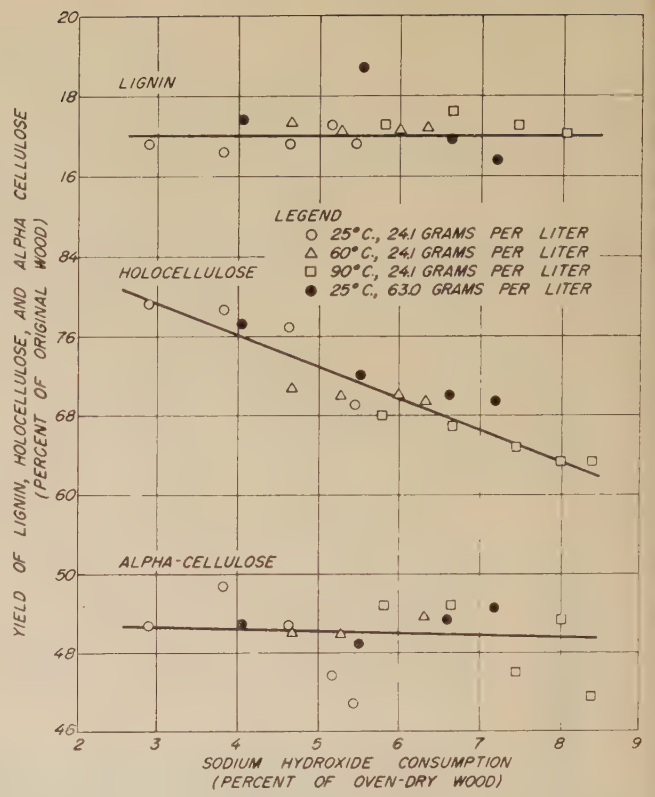

Fig. 4. Relation between chemical composition of aspen pulps and consumption of sodium hydroxide under several treating conditions

linearly with increase in alkali consumption. The scatter of points about the average line shows that this relationship is independent of temperature and alkali concentration. This meant that the loss in yield was due mainly to a loss in hemicellulose.

Strength Properties

Because the bulkiness of the pulps tended to increase with increasing yield and to decrease with the higher treating temperature, it was difficult to compare the strength properties of the more bulky pulps made in the highest yields at 25°C. with those of the denser ones made in the lowest yields at 90°C. on the basis of the same physical processing (measured by freeness) and equal test-sheet density. The strength data were therefore plotted on both bases, and the resulting curves are shown in Figs. 5 and 6. The relatively sharp maximums in bursting and tensile strength for the pulps made in yields near 91 or 92% with the weaker treating solution of 24.1 grams per liter, as shown by the curves plotted on an equal density basis (Fig. 5), may be partly due to bonding caused by the hydration produced by the beating of these pulps. On the other hand, when the variations in these strength properties are considered on the basis of equal freeness (Fig. 6), a constant value is approached at a yield near 90% even though the test sheets from the higher-yield pulps are much lower in density than those from the lower-yield pulps. In either case, a maximum in bursting and tensile strength appears to have been reached in pulps made in yields near 90% and no appreciable increase in these strength properties was associated with yields below this point. The tearing strength of the pulps also appeared to approach a maximum at this yield, although the results are not as outstanding as for

Table I. Conditions and Results of Mild Treatments of Aspen Chips with Sodium Hydroxide

Digestion No.	Treatment temperature, °C.	Treatment time, hr.	Caustic consumed Per cent of caustic charged, %	Per cent of oven-dry wood, %	Pulp yield, %	Yields of lignin and cellulose (based on original wood) Lignin, %	Holocellulose, %	Alphacellulose, %	Strength properties[a] At a sheet density of 0.60 g./cc. Bursting strength, pt./lb.	Tearing strength, g./lb.	Tensile strength, meters	Schopper-Riegler freeness, ml.	At 700 ml. Schopper-Riegler freeness Bursting strength, pt./lb.	Tearing strength, g./lb.	Tensile strength, meters	Density, g./cc
Treatments with 24.1 grams per liter solution[b]																
731	25	1/4	25.3	2.90	94.6	16.8	79.4	48.7	..	..	..	..	..	..	..	..
732	25	1/2	33.4	3.83	92.8	16.6	78.6	49.7	0.44	0.55	4000	300	0.20	0.84	2200	0.36
733	25	1	40.3	4.63	92.1	16.8	76.6	48.7	0.52	0.72	5000	410	0.32	0.88	3300	0.50
734	25	1 1/2	44.9	5.16	91.3	17.3	71.2	47.4	0.58	0.75	5050	430	0.31	0.93	3200	0.47
735	25	2	47.5	5.46	90.4	16.8	68.9	46.7	0.60	0.75	4750	380	0.38	0.88	3500	0.49
5446[c]	25	2	49.4	5.68	91.6	..	..	..	..	..	..	..	..	..	..	..
[d]	25	5	..	6.00	89.8	..	..	..	0.52	0.93	4020	..	0.43	0.90	..	..
807	60	1/4	40.6	4.67	91.5	17.3	70.3	48.5	0.49	0.89	4360	620	0.44	0.93	3750	0.55
808	60	1/2	46.0	5.29	90.5	17.1	70.0	48.5	0.52	0.81	4950	550	0.40	0.86	3800	0.53
809	60	1	52.3	6.00	90.2	17.1	70.0	50.4	0.50	0.95	4500	650	0.44	0.99	4300	0.58
810	60	2	55.2	6.34	90.2	17.2	69.5	48.9	0.47	0.95	4000	730	0.50	0.95	4200	0.63
[d]	60	5	..	6.40	88.0	..	..	..	0.41	0.91	3850	..	0.49	0.98	..	..
811	90	1/4	50.6	5.82	89.9	17.3	68.0	49.2	0.52	0.92	4400	660	0.49	0.96	4100	0.59
813	90	1/2	58.0	6.67	87.4	17.6	66.6	49.2	0.47	0.91	3890	700	0.47	0.91	3900	0.60
814	90	1	65.2	7.49	85.1	17.2	64.4	47.4	0.38	0.97	3500	790	0.54	0.96	4800	0.66
815	90	2	69.9	8.04	84.3	17.0	63.6	48.8	0.48	0.98	3800	740	0.54	0.99	4650	0.64
816	90	5	73.0	8.40	82.2	15.7	63.7	46.8	0.49	1.00	4400	740	0.54	1.02	4800	0.63
Treatments with 63.0 grams per liter solution[b]																
803	25	1/4	13.5	4.05	91.8	17.4	77.2	48.7	..	..	..	..	0.20	0.88	2100	0.41
804	25	1/2	18.4	5.52	90.3	18.7	72.0	48.2	0.46	0.80	4700	320	0.30	0.87	1800	0.45
805	25	1	22.1	6.63	88.8	16.9	70.0	48.8	0.54	0.88	4600	370	0.46	0.97	3700	0.52
806	25	2	24.0	7.20	88.4	16.4	69.5	49.1	0.57	0.91	4550	570	0.43	0.98	3600	0.54
[d]	25	5	..	8.00	86.9	..	..	..	0.52	0.98	4300	...	0.45	0.96	..	..
Treatment with disintegrated chips and 22.3 grams per liter solution[b]																
812	25	2	46.2	6.36	88.7	..	..	..	0.52	0.85	4900	580	0.37	0.88	3500	0.52
Fiberized, untreated chips (raw wood)																
..	..	.	..	..	95.3	17.7	78.6	48.6	..	..	..	..	0.046	0.15	330	0.31

[a] Ream size of 500 sheets—25 × 40 inches.
[b] Chemical ratios of 11.5, 13.8, and 30.0% of wood for treatments with 24.1, 22.3, and 63.0 grams per liter solutions of sodium hydroxide, respectively.
[c] 13-cubic foot digester used.
[d] Data by interpolation.

bursting and tensile strength. A possible explanation for these maximums is that this point also corresponds to the point of maximum swelling of the wood under the conditions used. At this point, the swelling might have weakened the fiber bonds in the wood, thereby permitting a relatively easy mechanical separation of the fibers without the physical disintegration obtained in a similar fiberizing of raw wood. Although hemicelluloses generally are related to pulp strength, their decrease with decreasing yield below 90% did not affect pulp strength within the range of the experiments.

These results indicate that the strength properties of the pulps made with the lower concentration of treating alkali were independent of the temperature of the treatment. The use of the higher concentration of 63 grams per liter for the treating solution caused a displacement of the maximums of the strength-yield relations toward a lower yield of roughly 88%. This displacement may have resulted because a greater loss of hemicelluloses occurred before the pulp attained maximum swelling than with the less concentrated treating solution.

From considerations of pulp yields and strength properties within the range of the experiments, it is indicated that pulp No. 735 (Table I) would be optimum for this process. This pulp was produced in a yield near 90% with a sodium hydroxide liquor of about 25 grams per liter and a treating time of 2 hours at 25°C. Although the important factor of energy for fiberizing the treated chips was not investigated in this study, the observation was made that the chips treated at 60 and 90°C. were more easily fiberized than those treated at 25°C. Obviously, the optimum combination of treating and fiberizing conditions and chemical, steam, and energy consumption must be determined in order to obtain the best results from the process.

The pulps made by the mild alkaline treatment under the above optimum conditions were 25 to 50% stronger than the strongest pulps made in a previous investigation with a steam cooking procedure (*2*). The pulp made under the mildest treating condition in these experiments (15 minutes at 25°C. with a caustic solution concentration of 24.1 grams per liter) was produced in a yield approximately the same as that obtained by fiberizing raw wood. The pulp made by the procedure described was, however, much stronger than that from raw wood (pulp No. 731 and "raw wood," Table I).

EFFECT OF CHIP SIZE

The standard 5/8-inch chips, which are approximately 5/8 inch in the grain direction, 1/8 inch thick, and 1/2 to 1 inch wide, were not completely penetrated when treated for as long as 5 hours at 25°C. with caustic soda solution in concentrations of 24.1 and 63.0 grams per liter. Small areas in the centers of a large number of the treated chips were bright and dry. Complete penetration was obtained, however, with the material that had been given a preliminary disintegration in the attrition mill (No. 812, Table I). The chemical consumption was higher than that for practically the same

Table II. Properties of Experimental Boards Made of Aspen Treated with Caustic Soda, as Compared with a Commercial Corrugating Board

Properties	Caustic-treated aspen corrugating board[a]	Commercial hardwood[b] corrugating board
Pulp yield, %	91.6	..
Properties of corrugating board:		
Weight, lb/1000 sq. ft.	25.4	27.4
Caliper, 0.001 in.	8.3	10.0
Density, g./cc.	0.59	0.53
Bursting strength:		
Mullen, pt	45.0	36.3
Unit, pt./lb./ream[c]	0.51	0.38
Tearing strength, g./lb./ream[c]	0.97	1.00
Tensile strength, lb./in. width	40.0	30.1
Stretch, %	2.1	2.0
Compression resistance, lb.	50.9	49.6

[a] Machine run 3177.
[b] Average of five commercial hardwood semichemical corrugating boards.
[c] 25 × 40—500 ream.

treatment with the standard chips (No. 735), and there was a corresponding decrease in pulp yield. The rate of chemical consumption was thus higher with the reduced-size material and was nearly the same as that obtained with the standard chips treated with the more concentrated alkali solution of 63 grams per liter (No. 806, Table I). The strength properties of the pulp from the reduced-size chips were also much the same as those of the pulp made in the same yield (No. 805) with the more concentrated treating liquor. Apparently, reducing the size of the chips made the hemicelluloses more available for solution. The results of the experiment with the reduced-size chips indicated that the lack of complete penetration of the standard chips was not serious with respect to strength.

It was observed that, after treatment, the reduced-size chips were more easily fiberized than standard chips comparably treated. Thus it is possible that there would be a saving in total energy consumption by preliminary partial disintegration since the energy consumed in this step is probably also low.

APPLICATION OF THE PROCESS TO CORRUGATING BOARD

The treating conditions considered to be optimum produced pulp of a quality in the range of that used for corrugating board. These conditions were applied in a larger-scale experiment with the purpose of producing a sufficient amount of pulp for a run of this kind of board on the experimental paper machine. The treatment was made with chips of standard size (No. 5446, Table I). The fiberizing of the treated chips in a machine of commercial size required about 26 horsepower-days per ton of pulp to produce a pulp with a freeness of 450 ml. (Canadian Standard). This energy value is well within the range of commercial practice. The yield of pulp was slightly higher than that obtained under the same conditions in the small-scale experiments, although the chemical consumption was much the same (Nos. 5446 and 735, Table I). The pulp strength was also in line with that of the small-scale pulp.

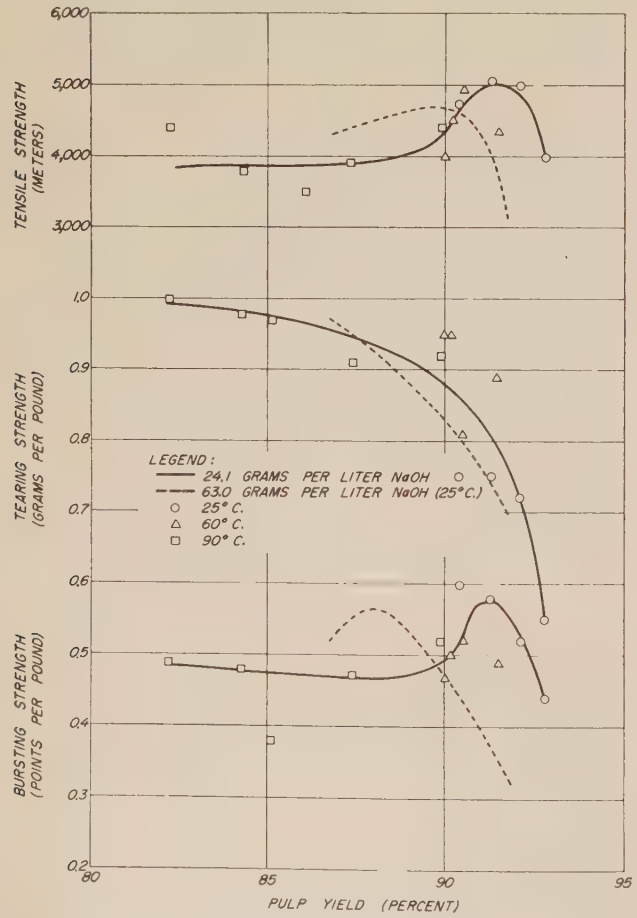

Fig. 5. Relation between pulp strength and yield of aspen pulp made by mild sodium hydroxide treatments at different temperatures and alkali concentrations (sheet density–0.60 g./cc.)

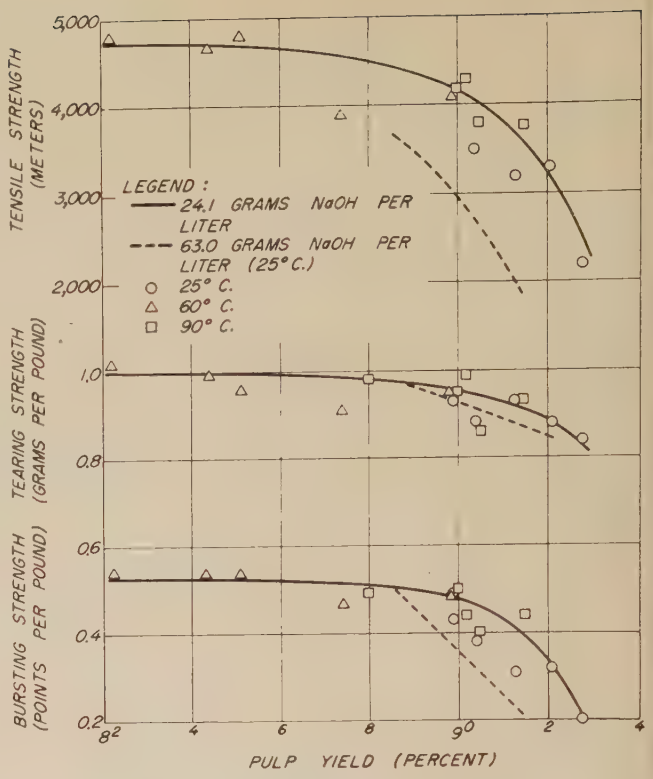

Fig. 6. Relation of yield and strength properties of aspen pulps made by sodium hydroxide treatment, when at 700 ml. freeness (Schopper-Riegler)

The properties of the experimental corrugating board are compared in Table II with average test values for commercial hardwood semichemical corrugating board. The experimental board compared favorably in almost every respect with the commercial board. It was also relatively light in color and had a brightness value of 46.1%. A corrugating test under commercial conditions, conversion of the material into container board, and tests on the containers would, of course, be needed for a complete evaluation of the material. The interesting point is that this high-yield pulp, made under relatively mild conditions at room temperature and pressure, has shown possibilities of being used in products normally made from lower-yield materials or from long-fibered woods. Undoubtedly, there are also other uses than corrugating board for pulps made by this process.

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The Effect of Fiber Characteristics on Paper and Papermaking Properties

Presentations at TAPPI-CPPA Fundamental Research Conference

THE Official Opening of the Fundamental Research Conference sponsored jointly by the Technical Association of the Pulp and Paper Industry and the Technical Section, Canadian Pulp and Paper Association, took place on Monday, May 29, 1950, in the Ballroom of the Chateau Frontenac, Quebec City, Quebec, Canada, commencing at 9:15 o'clock a.m.

E. G. KIRBY: Gentlemen, as Chairman of the Technical Section of the Canadian Pulp and Paper Association, it is particularly a pleasure for me to welcome all our foreign visitors to Quebec for this joint meeting of the Fundamental Research Committees of the Technical Section of the Canadian Pulp and Paper Association and the Technical Association of the Pulp and Paper Industry.

I do not intend to make a long speech this morning. You have a lot more interesting and more intelligent speakers to listen to within the next three days, but I just want to let you know that Dr. Gallay and Dr. Lewis are delighted to have so many people present. The program is the result of their joint efforts, and I am sure it will be enjoyed and have much value to all of you.

May I say, on behalf of the Technical Section, that I hope there are many of you who are planning to stay over for the three-day Conference of the Technical Section, itself, commencing Wednesday.

May I wish you all success in your endeavors and conferences during these first three days this week.

W. GALLAY: Gentlemen: Just a very few words, by way of introduction, before proceeding with the actual program.

As you know, this is a Fundamental Research Conference sponsored by the two Fundamental Research Committees, the Technical Association of the Pulp and Paper Industry and the Technical Section of the Canadian Pulp and Paper Association.

The Canadian Committee has, for several years, taken particular interest in the subject theme of the present conference and to us it is a temporary culmination of something we have looked forward to for a long time.

In a moment, Dr. Lewis will tell you how it fits in with TAPPI plans—that is, the plans of his Committee.

The subject we are going to discuss is an important one. We think it is the basic technical problem of our industries. It has a great many phases and, at the risk of being over ambitious, we have included these, in order to get a broad perspective of the whole subject. These topics have no solution at the moment, and in some cases, we have little knowledge of these topics which are going to have a number of considerations.

We certainly do not hope to expect to settle any of these matters at this meeting. We have two aims in general: one is to examine very carefully and critically the state of our knowledge and available data, and to correlate them as well as we can to one whole. And, secondly, we want to point up the gaps in our knowledge so that we will have a reasonably clear-cut guidance for future research.

We certainly hope and expect that all of you will partake fully in the discussions of questions; criticize, and express your views. I do not need to point out to you that a great deal of success in a meeting of this kind depends on the discussion.

Dr. Lewis, have you anything to add?

H. F. LEWIS: Not very much more, except to say that this meeting stemmed out of the Madison meeting of 1948 which had for its theme the Physical Components of Wood. Dr. Gallay and I happened, fortunately, to be assigned to the same room and, in those periods when we were together, we discussed what seemed to be indicated as the subject of our next meeting and how the two Fundamental Committees, above and below the border, could cooperate—and here we are.

This meeting is the fourth in a series. Some of you were at the first meeting of the series, held in Detroit in 1946, when we talked about Pulpwood and Pulpwood Stands. Following this we met in Appleton in 1947 and considered the Nature of the Chemical Components of Wood; then we held the Madison meeting of 1948, where we reviewed the Physical Properties of the Components of Wood.

We are going to try to achieve an atmosphere of perfect informality in the ballroom and that is not an easy thing to do. The surroundings will probably overwhelm you—you may find it difficult to imagine yourself sitting around a table but that is what you are doing. This is a Canadian meeting and I am not sure whether they use first names or not up here in Canada. If it were in Sweden, last names would be the style—below the border, first names are common. So you can take your pick and follow your own style—whether you are from Sweden, from the States, from Canada, or from the British Isles.

In the discussions, we are going to try to direct the thought, in so far as possible, to the material presented in the paper under discussion. It is going to be a difficult thing to do, because there is so much interrelationship between the subjects. However, if, following the first paper, we try to cover items which will appear later in the program, we will defeat our purpose.

There are some program changes. Unfortunately, Dr. Clark is ill and is not able to be with us. His paper will be included in the printed report of this meeting.

W. GALLAY: We will now proceed with the program of the first session, for which C. B. Purves, of McGill University is to be the discussion leader.

Effect of Variations in Size and Shape of Fibers on Papermaking Properties

GERALD HAYWOOD

The data presented in this paper are arranged in three broad sections: (1) a list of the variations in length of fibers from coniferous and deciduous woods. A classification of various deciduous woods according to the wall thickness of their libriform fibers. (2) Presentation of data to show how variations in fiber length and wall thickness affect such properties as tearing, bursting, and folding strength, bulk, and opacity. (3) Presentation of data to show that each of the process steps used to reduce wood to pulp plays an important role in determining the ultimate quality and papermaking properties of a pulp.

GERALD HAYWOOD, Member TAPPI; Project Director, West Virginia Pulp & Paper Co., Luke, Md.

TO HAVE a basis for discussing the effect of variations in size and shape of wood pulp fibers on their papermaking properties, it is necessary (1) to know what the variations are in wood pulps available; (2) to have pure pulps from each of the woods by the various processes used to reduce wood to pulp; (3) to have a method of measuring the fiber length distribution of these pure pulps; (4) to have a method of measuring the relative proportion of thin-walled springwood fibers and thick-walled summerwood fibers; and (5) to have a standard method of evaluating these pure pulps in terms of their significant papermaking properties which are tearing, bursting, and folding strengths, bulk, and opacity.

Table I. Bauer-McNett Classification

	On 20 mesh, %	*Through 20 on 35, %*	*Through 35 on 65, %*	*Through 65 on 150, %*	*Through 150, %*	*Estimted av. length, mm.*
			Coniferous pulps			
Red pine	23.0	39.9	23.5	6.3	7.3	1.73
White pine	63.9	15.9	9.7	3.3	7.2	2.23
Tyrone pine	49.6	22.4	15.2	6.0	6.8	2.04
Luke pine	55.4	18.2	13.7	5.4	7.3	2.11
Covington pine	68.7	15.1	8.7	2.6	4.9	2.34
Charleston pine	71.4	13.8	7.5	2.3	6.0	2.38
Hemlock	63.6	14.2	9.9	3.6	8.7	2.20
Mechanicville spruce	62.8	19.2	9.7	4.2	4.1	2.26
Swedish spruce	70.0	13.1	7.9	3.1	5.9	2.33
Douglas-fir	76.3	11.0	7.0	2.5	3.2	2.45
Swedish pine	62.8	19.2	9.7	4.2	4.1	2.26
Stora 32	68.8	15.7	7.9	3.5	4.1	2.34
Av. weighted length of fraction, mm.	2.81	1.90	1.18	6.7	...	...

Because such a large proportion of coniferous pulp fibers is caught on the 20-mesh screen of the Bauer-McNett classifier, it is necessary to use the 10, 14, 16 and 20-mesh screens to obtain data for the long fibers in coniferous pulps.

	On 10 mesh, %	*Through 10 on 14, %*	*Through 14 on 16, %*	*Through 16 on 20, %*	*Through 20, %*	*Estimated Av. length, mm.*
Stora 32	0.6	34.0	12.3	19.1	33.7	2.47
Husum pine	0.2	21.3	16.4	21.8	40.2	2.46
Mechanicville pine	23.4	31.2	6.8	11.7	23.9	2.83
Svartvik spruce	0.7	29.1	13.9	17.9	38.4	2.43
Tofte spruce	0.8	28.4	14.2	17.6	39.3	2.02
Parana pine	79.5	6.3	2.1	4.4	7.7	4.00
Av. weighted length of fraction, mm.	4.49	3.68	3.28	2.65	1.90	...

	On 20 mesh, %	*Through 20 on 35, %*	*Through 35 on 65, %*	*Through 65 on 150, %*	*Through 150, %*	*Estimated av. length mm.*
Birch	0.2	46.8	39.9	6.3	6.8	1.28
Gum	3.5	49.6	28.5	5.3	13.1	1.25
White oak	1.5	34.3	33.8	9.3	21.1	1.06
Rock oak	0.3	37.9	30.0	7.9	23.9	1.03
Poplar	0.1	7.0	62.1	20.2	10.6	1.01
Elm	1.9	33.4	29.1	7.2	28.4	0.98
Red oak	0.1	21.0	39.5	11.2	27.2	0.90
Beech	0.4	12.0	47.4	17.4	23.2	0.89
Water oak	0.9	26.1	33.7	10.4	28.9	0.91
Maple	0.1	0.3	49.2	32.8	17.6	0.83
Wild cherry	0.1	4.0	40.0	29.3	26.6	0.76
Birch from Sweden	0.6	24.3	55.1	11.4	8.6	1.14
50–50 Red and white oak	1.7	32.6	32.9	9.5	22.1	1.0
Fractionated red and white oak	3.2	40.9	36.2	10.2	7.5	1.23
Av. weighted length of fraction, mm.	1.97	1.61	1.20	0.72	...	...

Table II. Microscopic Measurement

Interval, mm.	*Douglas-fir*	*Western hemlock*	*Black spruce*	*Sitka spruce*	*Nicaraguan pine*	*Parana pine*
0.02–0.19	3.5	2.4	3.8	3.2	10.5	0.6
0.20–0.59	18.1	8.2	7.0	12.6	14.6	2.4
0.60–0.99	7.3	3.8	9.0	5.0	14.1	4.3
1.0 –1.39	9.2	2.7	8.8	5.5	7.1	2.9
1.4 –1.79	6.1	2.6	7.4	4.5	5.6	4.0
1.8 –2.19	12.3	10.5	13.3	8.4	5.6	6.3
2.2 –2.59	4.0	9.4	8.9	1.7	3.8	5.6
2.6 –2.99	4.7	9.3	15.1	5.8	3.5	6.3
3.0 –3.39	9.0	13.7	14.4	10.8	5.4	9.1
3.4 –3.79	1.6	5.9	1.0	6.0	6.1	7.4
3.8 –4.19	10.1	9.1	11.2	10.7	1.7	5.0
4.2 –4.59	5.6	8.7	...	6.0	5.5	4.8
4.6 –4.99	4.2	6.2	...	8.2	5.8	8.3
5.0 and over	1.2	7.5	...	9.4	10.7	32.9
Weighted av. length	2.20	2.94	2.17	2.88	2.27	4.01
Weighted av. width	0.034	0.038	0.030	0.038	0.036	0.036
Ratio: Length/Width	65	77	71	76	63	111

Interval, mm.	*Gum*	*Ash*	*Aspen*	*Cotton-wood*	*Elm*	*Sweet gum*	*Black oak*	*Pecan*	*Willow*
0.02–0.19	17.5	12.0	7.1	6.7	8.1	14.0	20.8	16.5	5.5
0.20–0.39	5.2	5.9	6.0	5.3	10.1	4.0	5.4	3.8	3.6
0.40–0.59	5.2	5.2	10.8	5.2	2.3	2.8	5.7	4.8	3.8
0.60–0.79	7.6	10.1	18.4	8.8	2.6	4.7	13.7	7.9	10.3
0.80–0.99	6.4	23.9	20.9	18.0	4.7	6.4	10.9	13.8	14.7
1.00–1.19	9.2	19.0	13.6	21.6	6.4	5.7	10.5	20.1	18.9
1.20–1.39	5.6	11.0	10.1	16.3	3.7	10.8	15.8	13.9	24.4
1.40–1.59	11.0	7.9	9.3	8.7	9.8	11.3	10.0	12.2	16.1
1.60–1.79	8.6	4.1	2.6	4.9	10.9	10.8	5.0	6.9	2.7
1.80–1.99	14.0	0.8	1.0	3.7	21.8	18.1	2.1	...	...
2.00–2.19	4.8	...	...	0.7	14.3	6.7	...	...	...
2.20–2.39	2.9	...	...	...	4.7	3.6	...	...	...
2.40–2.59	1.9	...	...	...	0.9	1.0	...	...	...
Av. length, mm.	1.40	0.90	0.88	1.02	1.29	1.28	0.93	1.03	1.05
Av. width, mm.	0.024	0.022	0.025	0.023	0.021	0.027	0.020	0.020	0.021
Ratio: Length/Width	58	41	35	44	61	48	47	51	50

Pure pulps have been obtained from various species of coniferous and deciduous woods by the sodium sulphite semichemical, full monosulphite, acid sulphite, and sulphate processes. The fiber length distribution of these pulps has been obtained by two methods: (1) by the Bauer-McNett fiber classifier (Table I) and (2) by use of the microscope (Table II). A correlation between the two methods was obtained by measuring, with the microscope, the fiber length distribution of the fractions of pulp retained on each screen of the Bauer-McNett

Table III. Proportion and Properties of Ray and Parenchyma Cells

	Through 150-mesh screen,
Coniferous Pulps	
Red pine	7.3
White pine	7.2
Pine from Tyrone	6.8
Pine from Luke	7.3
Pine from Covington	4.9
Pine from Charleston	6.0
Hemlock	8.7
Spruce from Mechanicville	4.1
Spruce from Sweden	5.9
Douglas-fir	3.2
Pine from Sweden	4.1
Stora 32	4.1
Deciduous pulps	
Birch	6.8
Poplar	10.6
Gum	13.1
Maple	17.6
White oak	21.1
Beech	23.2
Rock oak	23.9
Wild cherry	26.6
Red oak	27.2
Elm	28.4
Water oak	28.9
50–50 red and white oak (whole)	22.1
50–50 red and white oak (fractionated)	7.5

Table IIIA. Red Oak Cooked by the Sulphate Method

	Oven-dry yield (wood basis)	*Pulp tests*				
		K No.[a]	*Lignin, %*	*Pentosans, %*	*Ether extract, %*	*ACS viscosity,*[b] *sec.*
Long portion	40.6	14.2	1.2	21.4	0.5	684
Ray fibers	9.8	24.1	6.1	26.2	5.2	96
Whole portion	50.4	16.2	2.2	23.0	...	417

[a] The expression *K number* is used throughout this paper for permanganate ($KMnO_4$) number.

[b] This viscosity reading is in seconds when 2.0 g. are dissolved in 100 ml. of cuprammonium hydroxide. When 2.5 g. were used the solution of ray fibers was too dark to read.

Table IIIB. Acid-Hydrolyzed Red Oak Cooked by the Sulphate Method

	Oven-dry yield (wood basis)	*K No.*	*Lignin, %*	*Pentosans, %*	*ACS viscosity,*[a] *sec.*
Long portion	35.4	9.1	1.4	4.4	496
Ray fibers	10.1	15.5	4.8	6.3	61
Whole	45.5	10.4	2.0	4.4	234

[a] Viscosity values are on 2.0-g. sample.

Table IIIC. Chain-Length Distribution of Unbleached Pulps from Acid-Hydrolyzed Red Oak

Whole pulp av. D.P. 1394		*Long fiber portion* av. D.P. 1461		*Fine fiber portion* av. D.P. 1250	
%	*D.P.*	*%*	*D.P.*	*%*	*D.P.*
4.4	96	6.0	393	6.0	126–368
14.0	604–737	13.1	607–853	7.3	523–694
20.6	907–933	3.6	1052	21.1	1095–1170
51.0	1347–1352	20.4	1223–1290	65.5	1495–1620
10.00	1997	56.9	1554		

fiber classifier. The relative proportion of thick-walled and thin-walled fibers to be expected in a pulp from a given wood was estimated by examination of cross sections of the wood under a microscope (Table III). In evaluating the pulps for strength and other properties, the standard TAPPI Valley beater method of beating and sheetmaking was used. For each fifth beating a standard pulp was used.

Before presenting data obtained by the procedures outlined, the physical make-up of coniferous and deciduous woods are briefly considered.

Coniferous woods consist of over 90% fiber tracheids which have thin walls in the spring growth and thick walls in the summer growth. The relative proportion of these thin- and thick-walled fibers depends on seasonal growth conditions. There are less than 10% by weight of ray and parenchyma cells in coniferous woods.

Deciduous woods are much more complex than coniferous woods in that they contain several types of fibers, different in shape and length, which are the result of the function they perform in growing wood. The principal fibrous component of deciduous wood is the libriform fibers which make up 60 to 80% of the wood. The ray and parenchyma cell content varies widely with species and may exceed 30% in certain species. The pore vessels, which are characteristic of deciduous woods, make up about 10% of the wood by weight. Seasonal growth conditions do not have a marked effect on the thickness of the fiber wall in a deciduous wood. Some species are predominantly thick walled and some species are predominantly thin walled.

The surface areas of seven samples of ray fibers dried down from water and dried down from acetone were determined by low-temperature nitrogen adsorption in the region of 79°K. (Table IV). The samples were quite fluffy and, although the surface area was not inappreciable, the high specific volume necessitated the use of a very small weight of material for the determination so that the absolute amount of adsorbed gas was low and the attendant errors, as indicated by a spread of the data from the curve, were high.

Table IV. Surface Areas of Pulp Samples

Sample	*Weight used, g.*	*Vm cc. S.T.P.*	*Specific nitrogen surface area, sq. m./g.*
Ray cells from unbleached hardwood pulp from water	1.253	0.568	1.99
Ray cells from unbleached hardwood pulp from acetone	1.214	0.929	3.35
Ray cells from unbleached oak alpha from water	1.326	0.592	1.96
Ray cells from unbleached oak alpha from acetone	0.850	0.592	3.05
Ray cells from unbleached semichemical poplar from water	2.542	0.769	1.33
Ray cells from unbleached semichemical poplar from acetone	0.633	1.020	7.06
Ray cells from bleached hardwood pulp from water	1.631	0.901	2.42
Ray cells from bleached hardwood pulp from acetone	0.823	0.571	3.00
Ray cells from bleached hardwood pulp from water	2.923	2.13	3.19
Ray cells from bleached hardwood pulp from acetone	0.943	1.16	5.39
Ray cells from bleached oak alpha from water	0.930	0.455	2.14
Ray cells from bleached oak alpha from acetone	0.728	0.515	3.10
Ray cells from bleached semichemical pulp from water	3.441	0.893	1.14
Ray cells from bleached semichemical pulp from acetone	0.590	0.746	5.54

Discussion

1. The weighted average length distribution of coniferous fibers varies from 2.0 to 3.0 mm.
2. The ratio of length to width varies from 63 to 111.
3. The weighted average length distribution of deciduous pulps varies from 0.80 to 1.3 mm.
4. The ratio of length to width varies from 35 to 58.
5. Coniferous fibers deposit a large fraction on the 20-mesh screen of the Bauer-McNett fiber classifier which can be broken down to smaller portions by using 10, 14, 16, and 20-mesh screens.
6. The ray and parenchyma fiber portion of coniferous pulps is under 10%.
7. The ray fiber portion of deciduous pulps varies widely—from less than 10% to over 25%.
8. The fiber length distribution of coniferous fibers is very evenly spread over a wide range—i.e., there are no peaks in a graph of length against percentage.
9. There are two peaks in the fiber length distribution of deciduous fibers, one from ray fibers and one from libriform fibers.
10. The average length of pine fibers is higher in species from South Carolina than in species from Virginia or Pennsylvania.
11. Ray fibers contain a much larger proportion of lignin, pentosans, and extractives than the long fibers of deciduous pulps and are more difficult to purify in any bleaching sequence.
12. Ray cells are lower in viscosity and degree of polymerization than the long fiber portion of deciduous pulp.
13. Ray cells when dried down from water yield hard, dense, transparent sheets which have a much lower specific surface (by low-temperature nitrogen adsorption) than when dried down from acetone. When ray cells are dried down from acetone, a soft fluffy material results. Ray cells from semichemical poplar pulp when dried down from acetone have a high specific surface.

RATIO OF THICK-WALLED TO THIN-WALLED FIBERS

Measurements were made on photographs of cross-sectional dimensions of the fiber and the fiber lumen of 20 fibers for each species of wood by means of dividers. Measurements were made only on the larger fibers on the photomicrograph in order to insure measuring the central portions of the fibers. The measurements were made in both the radial and tangential directions and recorded as the average of the two. From these measurements the percentage of the fiber diameter occupied by the cell wall was computed, the cell wall thickness being taken as equal to the difference between the fiber diameter and the lumen diameter. The fraction of the cross-sectional area occupied by the cell wall was calculated by assuming the fiber section to be annular and using the average values of the fiber and lumen diameters (Table V). These values of the proportion of the diameter and of the cross-sectional area occupied by the cell wall were then used to classify the wood species according to the method of Mühlsteph. Because Mühlsteph used two methods for determining into which group a species will fall, a number of the species were classified in two different groups depending on which method was employed; such species are listed as transitional groups with both group numbers indicated.

Before any conclusions can be drawn from the data appearing in Table V, some thought should be given to its limitations. All the measurements on any one species were made on one photomicrograph. Since wood structure varies through certain limits from tree to tree and from one location to another within a single tree depending on growth conditions, the photomicrograph measured may or may not present a typical cross

Table V. Muhlsteph Classification of Wood Species Which Are Available

Wood species	*Av. fiber diam., mm.*	*Av. lumen diam., mm.*	*Linear % of cell wall*	*X-sectional area of cell wall ($X10^{-5}$ mm.^{2})*	*Areal % cell wall*	*Mühlsteph grouping*
Butternut (Juglans cinerea)	0.033	0.029	12.1	19.5	22.8	I
Basswood (Tilia americana)	0.024	0.020	16.8	13.8	30.6	I, III
Red birch (Betula nigra)	0.021	0.017	19.1	11.9	34.5	III
Cucumber tree (Magnolia acuminata)	0.029	0.023	20.5	24.5	37.3	III
Balsam poplar (Populus candicans)	0.029	0.023	20.5	24.5	37.3	III
Black willow (Salix nigra)	0.019	0.015	21.0	10.7	37.7	III
Yellow buckeye (Aesculus octandra)	0.026	0.020	23.1	21.7	40.8	III
Tupelo gum (Nyssa aquatica)	0.034	0.026	23.6	37.7	41.5	III
Black gum (Nyssa sylvatica)	0.028	0.021	25.0	26.9	43.8	III
Box elder (Acer negundo)	0.022	0.016	27.3	17.9	47.1	III
Yellow birch (Betula lutea)	0.020	0.014	30.0	16.0	51.0	III
Silver maple (Acer saccharinum)	0.020	0.014	30.0	16.0	51.0	III
Black maple (Acer nigrum)	0.016	0.011	31.2	10.6	52.7	III
Sugar maple (Acer saccharum)	0.016	0.011	31.2	10.6	52.7	III
Yellow-poplar (Liriodendron tulipifera)	0.025	0.017	32.0	26.4	53.8	III
Gray birch (Betula populifera)	0.021	0.014	33.3	19.2	55.5	III
Largetooth aspen (Populus grandidentata)	0.018	0.012	33.3	14.1	55.5	III
Trembling aspen (Populus tremuloides)	0.024	0.016	33.3	25.1	55.5	III
Slippery elm (Ulmus fulva)	0.0196	0.0128	33.7	17.3	57.3	III
Red gum (Liquidambar styraciflua)	0.020	0.013	35.0	18.1	57.8	III
Swamp white oak (Quercus bicolor)	0.017	0.011	35.3	13.2	58.1	III
Black locust (Robinia pseudoacacia)	0.017	0.011	35.2	13.2	58.1	III
Red maple (Acer rubrum)	0.019	0.012	36.9	17.0	60.1	III
Northern red oak (Quercus borealis maxima)	0.019	0.012	36.9	17.0	60.1	III
Sycamore (Platanus occidentalis)	0.021	0.013	38.1	21.4	61.7	III
Black cherry (Prunus serotina)	0.021	0.013	38.1	21.4	61.7	III
Butternut hickory (Hicoria cordiformis)	0.014	0.0086	38.6	9.6	62.2	III
Shagbark hickory (Hicoria ovata)	0.018	0.011	38.8	15.9	62.6	III
Black birch (Betula lenta)	0.020	0.012	40.0	20.1	64.0	III
Shellbark hickory (Hicoria laciniosa)	0.016	0.0095	40.6	13.0	64.9	III
White ash (Fraxinus americana)	0.017	0.010	41.2	14.8	65.4	III
Cottonwood (Populus deltoides)	0.024	0.014	41.6	29.8	66.0	III
Green ash (Fraxinus pennsylvanica lanceolata)	0.019	0.011	42.1	18.8	66.5	III
Swamp black gum (Nyssa biflora)	0.026	0.015	42.3	35.4	66.7	III
Paper birch (Betula papyrifera)	0.030	0.017	43.4	48.0	67.9	III
Swamp chestnut oak (Quercus prinus)	0.019	0.0097	48.9	21.0	74.0	III
Pignut hickory (Hicoria glabra)	0.018	0.009	50.0	19.1	75.0	III, IV
Mockernut hickory (Hicoria alba)	0.016	0.008	50.0	15.1	75.0	III, IV
Black oak (Quercus velutina)	0.017	0.0085	50.0	17.0	75.0	III, IV
Scarlet oak (Quercus coccinea)	0.019	0.009	52.6	22.0	77.6	III, IV
Chestnut oak (Quercus montana)	0.019	0.009	52.6	22.0	77.6	III, IV
Black ash (Fraxinus nigra)	0.019	0.009	52.6	22.0	77.6	III, IV
White oak (Quercus alba)	0.017	0.008	53.0	17.7	77.9	III, IV
Burr oak (Quercus macracarpa)	0.020	0.0094	53.0	24.5	78.1	III, IV
Water oak (Quercus nigra)	0.020	0.009	55.0	25.0	79.8	III, IV
Southern red oak (Quercus rubra)	0.018	0.008	55.6	20.4	80.3	IV
Willow oak (Quercus phellos)	0.0197	0.0086	56.4	24.6	80.9	IV
American elm (Ulmus americana)	0.012	0.005	58.4	9.4	82.6	IV
Blackjack oak (Quercus marilandica)	0.0156	0.0065	58.3	15.8	82.7	IV
Live oak (Quercus virginiana)	0.0186	0.0075	59.7	22.8	83.8	IV
Beech (Fagus grandifolia)	0.016	0.006	62.5	17.3	85.9	IV
Rock elm (Ulmus thomasi)	0.014	0.0049	65.0	13.5	87.8	IV
Pine springwood, species unknown	0.032	0.028	12.5	18.9	24.4	II
Pine summerwood, species unknown	0.024	0.012	50.0	33.9	75.0	II
Post oak (Quercus stellata)	0.017	0.0078	0.541	17.9	0.751	III, IV

section of the species. Although the size of the fibers may vary through appreciable limits, it is doubtful if the ratio of cell wall thickness to fiber diameter is greatly altered. The position of a species in Table V should be considered as describing the species at least to a first approximation. If more sections were cut and examined, the average values thus obtained might displace a species within a group but it is doubtful if it would be displaced from one group to another. The values obtained on pine check quite closely the average values obtained by the Forest Products Laboratory from measurements on 10 pine specimens in which the percentage of springwood varied from 40 to 81%.

Examination of Table V reveals that the greater proportion of deciduous wood species that grow in the Appalachian area are those having thick-walled fibers—viz., oak, hickory, beech, elm, and ash. The woods having thin-walled fibers are black and tupelo gum, box elder, red birch, basswood, yellow buckeye, butternut, balsam, poplar, cucumber tree, and willow. The woods which yield fibers with wall thickness intermediate the thick- and thin-walled fibers are: gray, black, and paper birch, aspen, yellow-poplar, sycamore, locust, and the maples.

Data of the Forest Products Laboratory on pine pulps containing various percentages of springwood (thin-walled) fibers showed that burst, tensile, and fold values improved with an increase in springwood content. The tear value seemed to be more closely related to the proportion of thick-walled (summerwood) fibers. By analogy, it would be expected that, as the percentage of thin-walled fibers was increased in a deciduous pulp,

Table VI. TAPPI Strength Tests

Wood	K No.	Viscosity	Time	Total Strength Values: Tear	Burst	Fold	Bulk	S.N.	Av. Fiber Length mm.
Unbleached coniferous sulphate pulps									
White pine	28.4	4900	163	396	382	5515	5.05	123.0	2.23
Red pine	23.3	8000	128	375	310	5500	4.86	112.6	1.72
Hemlock	21.3	2000	154	425	314	3140	5.75	115.4	2.20
Spruce	21.9	3100	111	351	351	4230	5.23	118.0	2.26
Tyrone pine	17.4	570	82	385	260	3330	5.07	104.5	2.04
Luke pine	17.3	827	106	370	277	4150	4.99	106.8	2.11
Covington pine	21.5	520	117	440	251	2570	5.33	107.0	2.34
Charleston pine	28.3	2900	190	485	304	3350	5.25	119.5	2.38
Average				403	306	3970	5.19	113.3	2.16
Unbleached deciduous sulphate pulps									
Birch	11.9	2895	70	341	290	2165	4.83	100.8	1.28
Fractionated oak	10.6	6380	92	478	205	1060	5.68	95.1	1.23
Whole oak	12.2	4540	77	419	189	970	5.54	87.3	1.01
White oak	14.9	2070	64	354	154	620	5.82	72.6	1.06
Rock oak	13.0	2380	55	306	149	760	6.07	70.0	1.03
Poplar	12.5	2740	82	295	201	1571	5.28	79.4	1.01
Elm	16.4	2020	65	397	200	665	6.20	84.2	0.98
Red oak	11.4	2895	68	386	197	785	5.85	83.9	0.90
Beech	11.9	2220	67	325	183	645	5.73	75.4	0.89
Maple	13.4	3240	84	304	186	1034	5.22	76.2	0.83
Average				361	195	828	5.62	82.5	1.02

the burst, tensile, and fold values should also increase. Thick-walled fibers are needed to maintain tear. As tear is closely related to bulk, thick-walled fibers should also yield papers with higher opacity values.

STRENGTH EVALUATION

The standard TAPPI T 200 m-45 Valley beater method was used. Each fifth beating was made on a standard pulp—Stora 32. The handsheets were formed and wet pressed according to TAPPI procedures, air dried, and tested at 50% R. H. and 73°F. Tear, burst, and fold values were plotted against Williams slowness and the values at 25, 50, 100, and 200 seconds Williams taken from the graph. The strength at each of these freeness values was calculated by the following formula:

$$\sqrt[3]{\text{tear} \times \text{burst} \times \log \text{fold}}$$

The summation of the strength values for 25, 50, 100, and 200 Williams slowness is called the *strength number*.

EFFECT OF WET PRESSING ON THE STRENGTH VALUES OF TAPPI HANDSHEETS

Two Valley beatings were made of each pulp and the samples from each 5-minute interval set aside. The two unbeaten samples were blended thoroughly and 12 handsheets made. The two 5-minute samples were treated in the same way, and so on through the series. Six sheets of each series were left unpressed and six were wet pressed twice at 60 p.s.i. according to TAPPI procedure. The air-dry sheets were tested at 50% R. H. and 73° F.

Relation Between Burst and Freeness Values of Valley Beater Refined Hardwood and Pine Pulps When the Wet Pressure is Varied

Hardwood pulps are deficient in burst values at low freeness. There is no combination of freeness and wet pressure (even zero wet pressure) which will give the specified burst and bulk values when hardwood pulp is used as a 100% component of the furnish. If bulk is disregarded, it is possible, by a combination of beating and pressure, to obtain a 100% hardwood board which equals a pine board in burst value.

For instance, by beating hardwood pulp to a freeness of 180 seconds Williams and wet pressing at 30 p.s.i. pressure, a hardwood board with a thickness of only 10 points but with a burst value of 122 points can be made. It is possible to make a pine pulp board with a burst value of 119 and a thickness of 16.9 points by beating the pine pulp to only 32 seconds Williams and subjecting it to no wet pressure.

The specifications for 16-point liner board call for a thickness of 0.016 inch, a weight of 42 pounds per 1000 square feet (139 pounds on the 25 × 38—500 sheet basis), and a burst value of 100 points. From the operating and cost viewpoint it is advantageous to achieve these specified values with refined (beaten) pulp as free as possible and with no overweight.

All the pulps prepared were evaluated by the Valley beater method. In this method the sheets at 40 pounds basis weight are wet pressed at 60 p.s.i. prior to drying. The effect of wet pressure on the burst value of beaten pulp and its relation to paper machine operating conditions are not known. In order to correlate laboratory test values with paper machine operating conditions, Valley beater refined hardwood and pine pulps were made into sheets weighing 139 pounds (basis weight of 16-point board). The hardwood and pine pulps were refined to various Williams freeness values. The wet sheets formed on the British sheet machine were pressed at 0, 15, 30, 45, and 60 p.s.i., dried, and tested for thickness, specific volume, and burst. The mill-made board was also tested for thickness, specific volume, and burst.

The data show that, as the pulp is beaten, there is a progressive increase in burst value with increasing Williams freeness. The data also show that when pulp at any freeness value is pressed there is an increase in burst value but the bulk decreases. Therefore, wet pressing is equivalent to beating but, as beating continues, there finally arises a condition where it is impossible to obtain the specified bulk even with no wet pressing. For hardwood pulps this condition is reached when hardwood pulp is refined to 90 seconds Williams. The relation between freeness, burst value, and the permissible wet pressure for refined hardwood pulps to

give the specified bulk (0.016 inch) is shown in Table IX.

The data also show the relationship between thickness and burst values for pine pulp refined to 7, 10, 17, and 32 seconds Williams freeness. As beating progresses and freeness increases, the burst value goes up but burst values for the beaten pine pulp are of a different order of magnitude than for beaten hardwood pulp. As pressure is increased at any given freeness value, the burst value also increases, but pine pulp is more sensitive to either pressure or refining than is hardwood pulp.

It is possible to obtain much higher burst values on pine pulp than on hardwood pulp and always at much lower freeness values. For instance, at 30 seconds Williams the burst value for hardwood pulp is 73 and for pine pulp 122 points. The relation between freeness, burst value, and permissible wet pressure to obtain the specified bulk and weight values on pine pulp is shown in Table X.

Hardwood pulp takes more beating and/or wet pressure to obtain the desired bulk than does pine pulp, but there is no combination of freeness and wet pressure that will yield the desired burst (100 points) at the specified bulk when using hardwood pulp. When using pine pulp the desired burst can be obtained at zero wet pressure when the pulp has been refined to less than 17 seconds Williams freeness.

The relation between freeness and permissible wet

Table VII. Strength Values of Unpressed and Pressed Sheets

Pressure, p.s.i.	Tear 0	Tear 60	Burst 0	Burst 60	Fold 0	Fold 60	Bulk 0	Bulk 60	Gurley Densometer 0	Gurley Densometer 60
					B.C. hardwood					
Unbeaten	59	100	5	17	0	10	3.73	1.66	1	2
25 sec.	87	83	13	26	2	20	3.12	1.52	1	4
50 sec.	91	74	21	36	5	40	2.58	1.43	1	13
100 sec.	90	64	28	42	17	160	2.23	1.35	12	62
200 sec.	84	59	34	44	42	190	1.95	1.28	40	270
Total	352	280	96	148	66	410				
					B.L. soda					
Unbeaten	59	85	6	17	0	10	3.21	1.52	1	3
25 sec.	72	85	10	23	2	10	2.95	1.47	1	4
50 sec.	89	78	23	37	10	70	2.32	1.33	2	15
100 sec.	88	68	32	42	30	200	2.00	1.25	7	100
200 sec.	78	61	37	48	70	320	1.71	1.19	35	400
Total	327	292	102	150	112	600				
					U.L. soda					
Unbeaten	51	93	6	16	0	0	3.51	1.60	1	2
25 sec.	73	93	11	24	2	20	3.23	1.52	1	4
50 sec.	90	82	22	34	6	50	2.56	1.37	2	17
100 sec.	93	76	32	42	19	120	2.11	1.30	4	46
200 sec.	84	67	39	48	66	350	1.81	1.24	27	92
Total	340	318	104	148	93	540				
					B.C.F. oak					
Unbeaten	47	96	3	8	0	0	6.85	1.87	0	1
25 sec.	138	135	23	36	10	30	2.78	1.60	1	2
50 sec.	150	120	31	49	10	150	2.28	1.47	2	5
100 sec.	140	111	38	55	30	400	1.91	1.40	4	77
200 sec.	121	101	40	61	90	620	1.72	1.32	21	210
Total	549	467	132	201	140	1200				
					U.L. pine					
Unbeaten	211	214	10	25	0	40	3.31	1.50	1	3
25 sec.	203	120	42	55	180	520	2.41	1.33	2	10
50 sec.	145	103	56	61	420	720	1.95	1.29	4	37
100 sec.	131	93	63	66	630	990	1.71	1.25	16	290
200 sec.	110	91	67	69	860	1440	1.53	1.21	95	1170
Total	589	407	228	251	2090	3670				
					B.L. pine					
Unbeaten	191	184	13	27	10	50	3.09	1.46	1	3
25 sec,	188	110	34	48	70	320	2.41	1.34	1	7
50 sec.	130	90	48	56	270	540	1.90	1.26	4	32
100 sec.	108	83	53	59	490	870	1.66	1.22	30	310
200 sec.	98	81	56	65	860	1200	1.48	1.18	117	1300
Total	524	364	191	228	1690	2930				
					B.C.K. pine					
Unbeaten	216	175	14	30	10	70	3.10	1.57	1	3
25 sec.	199	90	40	50	130	320	2.52	1.38	2	5
50 sec.	134	84	50	56	340	600	1.98	1.30	3	32
100 sec.	115	77	54	61	580	720	1.72	1.26	15	200
200 sec.	107	77	60	66	640	900	1.56	1.23	100	1130
Total	555	328	204	233	1690	2540				
					B.C.E. pine					
Unbeaten	168	255	12	27	0	40	3.66	1.54	1	2
25 sec.	183	117	60	65	710	870	2.06	1.35	2	10
50 sec.	166	106	66	70	860	1060	1.82	1.31	5	45
100 sec.	143	101	72	75	1180	1400	1.60	1.26	26	300
200 sec.	120	87	77	78	1450	1550	1.48	1.23	156	1500
Total	612	411	275	288	4200	4880				

					U.M. sulphite					
Unbeaten	137	119	10	19	0	10	3.13	1.38	1	6
25 sec.	123	88	19	27	10	20	2.45	1.29	1	18
50 sec.	101	70	27	35	20	70	1.95	1.21	5	51
100 sec.	83	62	29	38	50	150	1.60	1.13	24	550
200 sec.	71	57	33	38	80	220	1.33	1.08	140	620
Total	378	277	108	128	160	460				
					B.M. sulphite					
Unbeaten	114	108	11	21	0	10	3.20	1.43	1	5
25 sec.	109	74	22	35	10	60	2.51	1.30	2	14
50 sec.	91	60	30	43	20	160	2.02	1.20	4	150
100 sec.	75	55	38	47	140	570	1.68	1.14	40	450
200 sec.	62	50	46	50	180	660	1.52	1.10	180	>1800
Total	337	239	136	175	350	1450				
					U.F. pine 16					
Unbeaten	183	305	7	22	0	60	3.80	1.58	0	2
25 sec.	225	124	65	77	730	930	2.15	1.32	1	9
50 sec.	170	118	77	83	1000	1120	1.80	1.29	6	36
100 sec.	145	111	80	88	1250	1340	1.63	1.26	22	210
200 sec.	139	106	85	89	1460	1750	1.49	1.22	120	1470
Total	679	459	307	337	4440	5140				
					Stora 32					
Unbeaten	141	198	9	18	0	10	3.12	1.79	1	2
25 sec.	201	131	46	58	290	530	2.28	1.45	2	9
50 sec.	160	113	62	69	640	640	1.93	1.38	6	30
100 sec.	128	101	69	72	640	820	1.72	1.32	21	170
200 sec.	120	95	74	76	790	1000	1.59	1.26	90	480

Table VIII. Effect of Wet Pressure on Strength Values of TAPPI Handsheets, 0-200 p.s.i.

Beating time	*Williams freeness*		*Approximate pressure on sheets, p.s.i.* 0	12.5	25	50	100	150	200
					Stora 32 bleached sulphate				
		Bulk	3.18	2.16	2.04	1.84	1.60	1.50	1.41
		Tear	150	199	204	201	245	246	221
		Burst	11	16	17	20	26	28	32
0	11.7	Fold	0	10	10	10	30	40	60
		Break	14	23	24	28	33	38	41
		Densometer	1	2	2	3	4	6	7
		Nelson opacity	59	59	57	58	55	52	52
		Bulk	2.40	1.72	1.67	1.53	1.40	1.34	1.28
		Tear	260	212	196	181	167	153	135
		Burst	36	46	47	49	55	55	56
10	17.4	Fold	80	300	330	360	470	530	730
		Break	43	54	55	59	66	65	69
		Densometer	1	3	4	7	9	15	15
		Nelson opacity	52	50	50	49	44	43	43
		Bulk	2.09	1.58	1.53	1.42	1.34	1.28	1.26
		Tear	192	161	159	142	123	119	115
		Burst	54	61	62	64	65	67	70
20	31.3	Fold	430	540	510	660	690	840	920
		Break	64	75	80	82	86	85	87
		Densometer	3	9	10	16	26	42	58
		Nelson opacity	53	51	48	47	44	44	42
		Bulk	1.89	1.49	1.48	1.39	1.30	1.26	1.24
		Tear	146	124	128	116	119	106	110
		Burst	63	68	68	69	69	73	75
30	52.5	Fold	650	560	680	820	1070	1000	1420
		Break	76	87	86	86	83	89	88
		Densometer	4	17	19	38	75	89	100
		Nelson opacity	50	47	47	46	42	40	39
		Bulk	1.69	1.42	1.37	1.33	1.26	1.23	1.20
		Tear	150	112	114	105	103	96	98
		Burst	67	68	71	72	76	76	72
40	92.5	Fold	740	740	880	900	940	1080	1180
		Break	87	90	96	93	95	95	100
		Densometer	20	66	86	140	220	370	410
		Nelson opacity	44	42	42	38	36	35	34
		Bulk	1.60	1.36	1.32	1.28	1.22	1.19	1.17
		Tear	122	111	106	106	94	98	100
		Burst	75	79	80	77	82	79	85
50	157	Fold	790	830	710	1070	1170	1120	1610
		Break	93	101	100	102	103	100	102
		Densometer	60	220	340	540	750	1350	1110
		Nelson opacity	42	40	40	38	34	35	34
		Bulk	1.54	1.33	1.32	1.25	1.21	1.18	1.16
		Tear	120	102	101	98	95	93	88
		Burst	76	77	79	78	79	77	82
55	235	Fold	860	970	900	990	1320	1410	1910
		Break	100	104	99	101	105	106	101
		Densometer	110	370	380	830	1300	1800	1800
		Nelson opacity	42	40	40	38	36	36	34

Table IX. Hardwood Pulp Board at 139 Pounds and 0.016 inch Thickness

Freeness	*Burst*	*Wet pressure, p.s.i.*
10	37	30
17	54	20
27	70	12
40	80	8
60	82	3

pressure to obtain the desired bulk and burst values on pine pulp is as follows:

Freeness	*Pressure, p.s.i.*
7	Over 60
10	20
17	none
32	none

FIBER LENGTH DISTRIBUTION OF BEATEN PULPS

The Bauer-McNett fiber classifier was used to follow the effect of beating on fiber length distribution. The data are given in Table XI.

OPACITY OF BLEACHED CONIFEROUS AND DECIDUOUS PULPS

The relation between opacity and weight of pine and hardwood TAPPI handsheets is shown in Table XII.

The relation between opacity and wet pressure applied to TAPPI test sheets is shown in Table XIII.

The relation between opacity, brightness and Williams freeness is given in Table XIV.

The relation between opacity of TAPPI handsheets and Williams freeness is shown in Table XV.

Table X. Pine Pulp Board at 139 lb. and 0.016 inch Thickness

Freeness	*Burst*	*Wet pressure, p.s.i.*
7	58	39
10	97	18
17	115	10
32	122	3

Discussion

Strength. The data show:

1. Pulps from coniferous woods have an average fiber length of 2.16 mm. Pulps from deciduous woods have an average fiber length of 1.02 mm. Deciduous pulps vary more in fiber length from species to species than do coniferous pulps.

2. Coniferous pulps require more beating time (or power) to develop strength than do deciduous pulps.

3. Coniferous pulps have distinctly higher strength values than do deciduous pulps, particularly in fold.

4. Coniferous pulps yield sheets of higher bulk (lower density) than do deciduous pulps.

5. The average strength value of all coniferous pulps is 113.3 with an average fiber length of 2.16. The average strength value of all deciduous pulps is 82.5, with an average fiber length of 1.02. Thus, it can be seen that the greater strength of coniferous pulps is related to but is not a linear function of fiber length.

6. Of the deciduous woods, birch yields pulp with the highest strength value. This higher strength, particularly in burst and fold values, is due in part to the fact that all birch fibers have thin walls.

7. The effect of removing a large proportion of the ray fibers from an oak pulp results in an increase in fiber length from 1.01 to 1.23 mm. The tearing strength is thus increased from 419 to 478, the burst from 189 to 205, and the over-all strength from 87.3 to 95.1. This illustrates the effect of fiber length on tearing strength.

Table XI. Fiber Length Distribution

	Unbeaten 25	*Beaten to 25 williams*	*Beaten to 50 williams*	*Beaten to 100 williams*	*Beaten to 200 williams*
		Hardwood alpha			
Tear	11	14	20	25	29
Burst	0	0	0	1	5
Fold	0	0	0	0	0
Per cent on 20 mesh	0.7	0	0	0	0
Per cent on 35 mesh	12.7	9.0	3.0	1.0	0
Per cent on 65 mesh	31.8	32.0	25.0	27.0	14.8
Per cent on 150 mesh	26.4	28.0	26.0	22.0	27.6
Per cent through 150 mesh	28.4	33.0	46.0	50.0	57.6
		Sulphate maple			
Tear	55	71	76	74	65
Burst	17	27	41	51	57
Fold	0	10	90	390	1300
Strength No.	...	12.4	18.3	20.8	22.6
Per cent on 20 mesh	0	0	0	0	0
Per cent on 35 mesh	0	0	0	0	0
Per cent on 65 mesh	61.9	60.0	56.0	53.5	46.1
Per cent on 150 mesh	24.6	24.0	27.0	28.5	30.0
Per cent through 150 mesh	13.3	16.0	17.0	18.0	23.6
		Sulphate pine			
Tear	156	117	107	102	97
Burst	9	57	62	66	70
Fold	10	720	980	1300	1750
Strength No.	...	26.7	27.1	27.6	28.0
Per cent on 20 mesh	55.7	49.0	47.0	44.0	41.0
Per cent on 35 mesh	24.4	23.0	22.0	21.0	20.0
Per cent on 65 mesh	12.3	14.5	16.0	16.0	16.0
Per cent on 150 mesh	3.9	5.0	6.0	7.5	9.0
Per cent through 150 mesh	3.7	8.5	9.0	11.5	14.0
		Unbleached spruce sulphite			
Tear	115	93	83	76	67
Burst	16	40	50	58	62
Fold	10	190	380	570	670
Strength No.	...	20.4	22.0	23.0	22.7
Per cent on 20 mesh	62.7	42.0	33.0	31.0	30.0
Per cent on 35 mesh	18.5	23.0	31.0	19.0	15.0
Per cent on 65 mesh	8.4	19.0	25.0	23.0	23.0
Per cent on 150 mesh	4.0	8.0	9.0	12.0	14.0
Per cent through 150 mesh	6.7	8.0	12.0	15.0	18.0

Table XII. Relation Between Opacity and Basis Weight

	Weight, lb./ream	Opacity, %	TAPPI bulk cc./g.
	Bleached hardwood pulp		
Unbeaten	26.9	55	1.66
	34.7	61	1.65
	41.8	67	1.64
	48.5	70	1.65
	55.0	73	1.65
	72.1	79	1.67
Beaten to 48 seconds Williams	34.4	59	1.48
	37.9	62	1.46
	41.6	64	1.44
	45.4	66	1.43
	50.0	69	1.40
Beaten to 158 seconds Williams	34.2	56	1.24
	37.9	58	1.22
	40.8	59	1.21
	45.1	63	1.20
	48.7	64	1.19
	Bleached pine pulp		
Unbeaten	27.0	44	1.58
	34.9	55	1.50
	42.1	60	1.46
	48.7	64	1.49
	55.8	67	1.50
	70.4	73	1.49
	84.0	77	1.50
Beaten to 51 seconds Williams	34.5	47	1.32
	37.6	50	1.28
	41.8	53	1.27
	45.1	54	1.26
	48.8	56	1.24
Beaten to 205 seconds Williams	34.3	43	1.21
	37.8	45	1.19
	42.0	48	1.15
	44.4	49	1.16
	49.5	52	1.14

8. The strength values obtained on poplar wood (which consist of thin-walled fibers) check the conclusion given for birch wood. The burst and fold values of pulps from thin-walled fibers are generally higher than from those with thick-walled fibers, such as the various oak woods. Pulps consisting of thick-walled fibers tend to give high tear values.

9. Deciduous pulps are characterized by their tendency to begin at a low tearing strength, to develop a maximum during the first half of the beating (25 to 50 seconds freeness), and to lose strength rather rapidly during the remainder of the beating period.

10. In contrast, coniferous pulps begin at maximum tearing strength and lose it rapidly at the start of the heating, and more gradually as beating proceeds.

Effect of Wet Pressure. The effect of no wet pressure and 60 pounds wet pressure on the strength values of TAPPI handsheets may be briefly summarized as follows:

1. With deciduous pulps, it is possible at low-freeness values, even with unbeaten pulp, to obtain higher tear values by wet pressing at 60 pounds pressure.

2. Both beating time and wet pressure at 60 pounds are required to develop the burst and fold values of deciduous pulps.

3. Fractionated oak pulp yields fairly high tear-value sheets at 25 seconds Williams whether wet pressed or not but, at higher freeness values, the tear value is sensitive to wet pressing.

Table XIV. Relation of Opacity, Brightness, and Freeness

Brightness, %	Unbeaten	Opacity, % Williams freeness, sec. 25	50	100	200
	Hardwood pulp				
37	84	81	79	77	75
54	74	72	69	67	64
64	69	68	66	64	63
68	70	67	65	63	61
71	69	67	65	63	60
73	68	67	65	63	60
74	70	67	65	63	61
76	68	66	64	63	60
	Pine pulp				
25	82	75	72	70	68
41	70	61	58	55	53
52	64	57	54	50	49
62	64	55	50	49	47
68	62	53	50	48	45
70	62	54	50	48	45
74	61	54	51	48	45

4. Coniferous pulps when unbeaten yield handsheets which have very high tear values whether wet pressed or not pressed. However, as soon as beating has progressed to where the slowness value is only 25 seconds Williams, the tear value is much lower if wet pressing is used. This decrease in tear values holds for all freeness values when the handsheets are wet pressed. Coniferous pulps are very sensitive to wet pressure, particularly in tearing strength.

5. As beating progresses, the burst value of coniferous pulps continually increases whether or not wet pressure is applied. The combination of beating and wet pressure yields the maximum burst values.

6. Hardwood pulps cannot yield a 16-point board which meets bulk and burst specifications, no matter how beaten or wet pressed. Pine pulp will yield a board which meets bulk and burst specifications when beaten to only 32 seconds Williams with no wet pressure.

7. The use of high wet pressures in the press section of a paper machine, particularly on deciduous pulps consisting largely of thick-walled fibers (such as oak) would permit development of tearing and bursting strength at high speed, because of the possibility of running free stock on the wire.

Effect of Beating on Fiber Length Distribution. When beating pulp in a Valley beater, the very long fibers are cut into shorter lengths. The proportion of fibers of intermediate length is not much changed by beating. The proportion of "fines" increases as beating progresses. An alpha pulp which did not hydrate yielded a powder in the beater with the result that the "fines" were doubled.

Opacity of Bleached Coniferous and Deciduous Pulps. The outstanding difference between coniferous and deciduous pulps is the greater bulk and opacity of deciduous pulps. The difference (when comparing pine and mixed hardwoods) is 6 to 7 points and holds over a wide paper weight, freeness, and brightness range.

EFFECT OF CHIPPING

Cook 117 was made on small hardwood chips received from the Covington experimental plant. Cook

Table XIII. Relation Between Opacity and Wet Pressing

Gage pressure TAPPI press	Hardwood Weight, lbs./ream	Hardwood Opacity, %	Hardwood Bulk, cc./g.	Pine Weight, lb./ream	Pine Opacity, %	Pine Bulk, cc./g.
20	40.0	68	2.06	42.3	62	1.87
40	40.1	66	1.77	41.3	59	1.59
50[a]	41.3	65	1.63	41.9	58	1.52
60	41.4	65	1.57	41.6	59	1.44
70	40.9	65	1.53	41.8	57	1.41
80	40.9	64	1.47	41.9	57	1.36
100	41.3	61	1.39	42.1	55	1.33
120	41.1	60	1.35	42.4	54	1.26

[a] Standard gage pressure for TAPPI method.

Table XV. Relation of Opacity and Freeness

Williams freeness	Unbeaten	Williams freeness, sec. 1.25	25	50	75	100	200
			Coniferous				
C. K. Pine	53	52	46	43	41	40	38
L. Pine	55	55	50	45	43	42	39
E. Pine	53	47	42	39	38	37	36
Stora 32	62	60	52	48	47	46	44
			Deciduous				
C. Hardwood	60	..	59	56	55	53	52
L. Hardwood	60	..	59	55	54	53	51
E. W. Oak	59	58	55	53	51	50	48
E. F. Oak	58	55	52	49	48	47	45

118 was made on chips received from the Charleston mill chipper. The relevant data are summarized in Table XVI.

These data show the effect of chip size on pulp yield and pulp quality. The large mill chips yield a very raw pulp with excessive screenings and the screened pulp has a K No. 7 points higher than the screened pulp from the small chips. The total yield of pulp is less from the large chips than from the small chips.

Note the much greater tear value of the better-cooked pulp from the small chips. This higher tear value is responsible for its higher strength index.

EFFECT OF COMPRESSION

Compressed and uncompressed chips were cooked in the laboratory digester and in baskets hung in large digesters. The pulp from the laboratory cooks was analyzed and evaluated for strength by the standard TAPPI procedures, both before and after bleaching. The unbleached pulp from the baskets was also evaluated by the TAPPI procedures and by a special procedure to ascertain the suitability of the pulp for manufacture into 16-point board.

Compression produced a visual change in the pine chips, in that they could be stretched like accordions. The data show that these compressed chips, because of the greater surface exposed, reacted much more rapidly with the chemicals in the cooking liquor to yield a pulp with less screenings, less lignin, and lower K No. than did pulp produced from uncompressed chips, both in the laboratory cooks and in the mill cooks. In studies of hardwood made some years ago, small hardwood chips from the 10-knife chipper in the pilot plant were compared with the large hardwood chips from the mill chippers. This comparison showed that the smaller chips also reacted more rapidly with the cooking liquor to yield a pulp lower in screenings and K No. than pulp from the larger chips. The strength data for the pulp from the large and small hardwood chips showed that the pulp from the small chips was higher in strength—particularly in tear—than the pulp from the large chips.

The strength data obtained on the pulps from the compressed and uncompressed pine chips are at variance with the data obtained on the small and large hardwood chips in that compression has produced a profound effect on the chips that goes beyond the rate of cooking resulting from the greater surface exposed.

Table XVI. 2¾ Hr. Cook—25% Sulphidity

Cook	Chips	K No.	Screenings, %	Screened pulp, %	Total yield, %
117	Small	17.2	0.9	50.8	51.7
118	Large	24.3	5.8	45.0	50.8

Table XVII. Total TAPPI Strength of Pulps

	Time	Tear	Burst	Fold	Bulk	S.N.
117	79.0	435	197	1080	5.73	90.0
118	69.5	338	195	980	6.11	82.9

All pulps from compressed chips, whether cooked in the laboratory or mill, unbleached or bleached, were definitely lower in strength than similar pulps from uncompressed chips. The difference was approximately 15% which was spread equally over tear, burst, fold, and tensile values. The special evaluation for suitability of the pulps in the manufacture of 16-point board, where only the burst test is made, showed a value of 160.5 for the pulp from the uncompressed chips and 134.5 for the pulp from the compressed chips. The difference of 26 points represents a loss of 16% in this value.

When the compressed and uncompressed chips were cooked in the laboratory under the same conditions, the compressed chips were more easily reduced to pulp. They consumed more alkali, yielded less screening, and produced a more thoroughly cooked pulp of lower permanganate number and viscosity than did the uncompressed chips. This is shown in Table XVIII.

A comparison of the strength values (Table XIX) of these pulps at equivalent permanganate numbers and 75 seconds Williams freeness shows that the compressed chips yield weaker pulp.

The strength indices also indicate that the unbleached pulp from the compressed chips is weaker.

$$\frac{\text{Strength index of compressed (II) } 103.6}{\text{Strength index of uncompressed (III) } 120.0} \times 100 = 86\%$$

$$\frac{\text{Strength index of compressed (IV) } 99.8}{\text{Strength index of uncompressed (V) } 118.3} \times 100 = 84\%$$

The pulps from cook III (uncompressed) and cook II (compressed) were bleached to a brightness of 76.0 to 77.2% and those from cook V (uncompressed) and IV (compressed) were bleached to 81.8 to 82.8%.

The TAPPI strength values at 75 seconds Williams freeness are listed in Table XX. The bleached pulps from the compressed chips are not as strong as those from the corresponding uncompressed chips.

The strength indices also show that the bleached pulp from the compressed chips is weaker than that from the corresponding uncompressed chips.

$$\frac{\text{Strength index of compressed (II) } 91.7}{\text{Strength index of uncompressed (III) } 105.1} \times 100 = 87\%$$

$$\frac{\text{Strength index of compressed (IV) } 78.4}{\text{Strength index of uncompressed (V) } 84.6} \times 100 = 93\%$$

EFFECT OF PROCESS STEPS ON QUALITY COOKING—SULPHITE VS. SULPHATE

A mixture of spruce, balsam, and hemlock chips was cooked by the acid sulphite and sulphate processes, and the two pulps were evaluated for strength, before and after bleaching, by the standard TAPPI method. The data are given in Table XXI.

Note that the unbleached kraft pulp is 20% higher in total strength than the unbleached sulphite pulp, the

Table XVIII

Cooking temp., ° C.	Screenings (based on screened pulp), Uncomp.	Comp.	K No. Uncomp.	Comp.	Viscosity, cp. Uncomp.	Comp.
160	6.58	2.24	27.8	21.6	5300	738
165	4.18	2.19	21.1	17.5	1040	331
170	3.75	..	17.2	..	292	.

Table XIX. Properties of Unbleached Pulps

No.	Kind of chips	K No.	Beating time, min.	Tear	Burst	Fold	Break	S.N.
III	Uncomp.	21.1	42	127	74	860	92	30.2
II	Comp.	21.6	39	116	59	450	75	26.3
V	Uncomp.	17.2	35	127	68	970	86	29.6
IV	Comp.	17.5	36	113	55	400	75	25.3

Table XX. Properties of Bleached Pulps

No.	Kind of chips	Brightness, %	Beating time, min.	Tear	Burst	Fold	Break	Opacity, %	S.N.
III	Uncomp.	77.2	24.0	102	66	430	80	46	26.1
II	Comp.	76.0	23.0	95	54	320	73	48	23.4
V	Uncomp.	81.8	14.5	77	50	330	64	48	21.2
IV	Comp.	82.8	15.5	81	42	160	61	48	19.6

Table XXI. Comparison of Sulphite and Kraft Pulps

	Sulphite		Kraft	
	Unbleached	Bleached	Unbleached	Bleached
K No.	10.9	...	18.2	...
Viscosity, cp.	1189	620	1345	362
Brightness, %	...	72.2	...	72.7
Total beating time, min.	57	58	103	75
Total tear	291	320	413	420
Total burst	306	300	349	346
Total fold	4050	4590	5340	5430
Total bulk	4.69	4.59	4.90	4.81
Strength index	101.8	105.1	121.8	121.1
% oven-dry pulp	44.4	...	45.7	...

result of higher tear and burst values. Note also that the kraft pulp requires more power to beat it whether bleached or unbleached.

Data for sulphate, monosulphite, and semichemical bleached birch pulps are given in Table XXII.

The atmospheric pulping of original and acid-hydrolyzed red oak by a chlorite-sodium hydroxide sequence was also studied.

Pulp A was prepared from original red oak chips. Pulp B was prepared from red oak chips hydrolyzed for 9 hours at 100°C. with 3.0 g.p.l. hydrochloric acid. Pulp C was oak pulp taken from mill digesters.

The analytical values for these pulps are shown in Table XXIII.

These three pulps were tested for strength by the ball mill method. In this method heavy sheets (110-pound basis) are made but are not subject to wet pressure. The results are presented in Table XXIV.

EFFECT OF CONCENTRATION OF COOKING LIQUOR ON THE SULPHATE COOKING OF BIRCH

Three cooks on birch were made to determine if variations in the initial concentration of the cooking liquor have very appreciable effects on the quality of

Table XXII

	Semi-chemical	Mono-sulphite	Sulphate
Brightness	79.2	81	82
Viscosity	210	55	930
Alpha-cellulose	73.1	75.5	...
Soluble in hot 3% NaOH	23.1	19.7	10.0
Yield (on oven-dry wood)	59.1	49.8	49.9
	Valley beating		
Beating time, min.	10	10	24
Williams freeness	324	172	200
Tear	53	52	76
Burst	70	66	77
Fold	1720	710	880
Bulk	1.05	1.16	1.14
Porosity, sec.	>1800	1105	...
S.N.	22.9	21.4	25.8

Table XXIII. Red Oak Pulp

	Oven-dry yield, %	K No.	Pentosans, %	Alpha-cellulose, %	ACS viscosity, sec.
A	51	4.3	27.3	85.0	1740
B	44	2.8	11.0	87.1	668
C	..	10.6	21.2	82.7	37

the unbleached pulp. The initial concentrations used were 20 g./l., 50 g./l., and 80 g./l. active Na_2O, maintaining a constant chemical charge on the wood (20% Na_2O), keeping the volume of liquor constant (24 liters) and varying the weight of chips. At a maximum temperature of 160°C. and with liquor of 26.3% sulphidity, the chips were reduced to pulp of K No. 11 to 13 by varying the time: 7 hours for the 20 g./l., 4 hours for the 50 g./l., and 3.5 hours for the 80 g./l. liquor.

There was a gradual fall in viscosity of the unbleached pulps as the initial liquor concentration was raised from 20 to 80 g./l.

No significant differences in the physical properties of the unbleached pulps produced at 20 and 50 g./l. Na_2O were evident. The data lead us to believe that these two samples are in the maximum range, so far as the over-all strength of unbleached birch pulp is concerned. Both have a strength index of 100. The unbleached stock from the 80 g./l. cook, however, was somewhat harder to beat, higher in tear and lower in burst, break, fold, and over-all strength index (96).

These results would indicate that little advantage is to be gained by using a liquor lower in initial concentration than 50 g./l., but that 80 g./l. may possibly be on the high side. It must be remembered that greater dilution takes place during cooking in the small digester than in a larger digester. The data in Table XXV

Table XXIV. Strength Properties of Red Oak Pulps

	Beating time, hr.	Williams slowness	Tensile breaking length, meters	Tear	M.I.T. double folds
Pulp A (original chips)	0	10	2	14	1
	1	81	42	76	50
	2	226	74	95	385
	3	524	89	75	565
	4	1011	101	60	1293
Pulp B (from acid-hydrolyzed chips)	0	14	2	6	0
	2	46	24	40	2
	4	383	38	36	2
	6	853	47	25	1
	8	180	39	21	1
Mill oak pulp	0	30	5	25	0
	2	76	27	72	20
	4	203	50	69	96
	6	704	57	63	283
	8	1047	54	54	59

Table XXV. Cooking Data

No.	Active Na_2O, g./l.	Ratio chips to liquor	Time, hr.	Oven-dry yield, % Screenings	Pulp	K No.	Viscosity, cp. (Luke)	Black liquo. Diln.	Active Na_2O, g./l.
55	20	1:10	7	1.1	41.4	12.2	4140	1.94	2.7
45	50	1:4	4	0.5	50.1	12.3	3141	1.77	8.5
56	80	1:2.5	3.5	0.6	50.1	11.9	1930	1.86	14.1

Luke strength test data (unbleached pulps)

No.	Active Na_2O, g./l.	Min. to 100 sec. freeness	Total strength values, 25, 50, 100, 200 freeness: Tear	Burst	Break	Fold	Strength index
55	20	21	327	274	403	3070	100
45	50	20	331	277	403	3060	100
56	80	23	344	244	357	2480	96

Table XXVI. Cooking Data

No.	Active Na_2O %: %	Active Na_2O %: g./l.	Oven-dry yield, % Screenings	Pulp	K No.	Viscosity, cp. (Luke)
41	20	50	1.0	52.0	13.1	8375
58	40	100	0.3	46.0	7.0	517

Luke strength test data

No.	Active Na_2O, %	Min. to 100 sec. freeness	Total strength values, 25, 50, 100, 200 freeness: Tear	Burst	Break	Fold	Strength index
41	20	19	314	252	378	1880	93
58	40	32	381	176	276	490	82

were obtained under the following conditions: maximum temperature, 160°C.; 20% Na_2O on chips; 24 liters liquor at 26.3% sulphidity. The weight of chips, concentration, and time were varied; the pulp was cooked to a K No. of 11 to 13.

EFFECT OF INCREASING (DOUBLING) THE CHARGE OF ACTIVE CHEMICALS

These two cooks on birch (data in Table XXVI) show the effect of high chemical charge and high concentration. Both cooks were made at a maximum temperature of 145°C. for 7 hours with a liquor of 25.4% sulphidity. One contained the normal chemical charge on the wood—20% Na_2O at 50 g./l. initial concentration. The other contained twice this amount or 40% Na_2O at a concentration of 100 g./l.

As might be expected, the unbleached pulp from the first cook at normal concentration produced bleachable pulp (K No. 13.1) of high viscosity (8375 cp.), where as the second cook at double the usual concentration gave a very easy bleaching pulp (K No. 7.0) of low viscosity (517 cp.).

The two unbleached pulps differ greatly in their strength characteristics. Judging by tear values alone, the low viscosity, easy bleaching pulp prepared with very strong liquor is much stronger than the high viscosity stock. On the other hand, the weak liquor cook produced a higher yield of pulp, which was easier to beat and had higher burst, break, fold, and over-all strength index. The cooking conditions were: maximum temperature 145°C., 6 kg. chips, 24 liters liquor, 25.4% sulphidity, 7-hour cooks.

EFFECT OF TEMPERATURE

The effect of the temperature of cooking hardwoods (2/3 gum, 1/3 oak) on pulp yield, K No. and viscosity is illustrated in Table XXVII.

These data show that, when the percentage of Na_2O on the hardwood chips is held at 18% and the maximum temperature of cooking is varied, the viscosity value, K No., and yield of screened pulp decrease regularly with increase in cooking temperature. On the basis of yield and viscosity value, the optimum temperature of cooking hardwoods is in the 150 to 160°C. zone.

The effect of increasing the cooking temperature, when birch, maple, poplar, and mixtures of the three woods are pulped by the sulphate process, is shown in Table XXVIII. The usual conditions apply to these cooks: 20% Na_2O on the wood, 50 g./l. Na_2O initial concentration, 25.4% sulphidity, and 7 hours.

Increasing the temperature, with cooking time constant, causes the viscosity of all pulps to fall. The over-all strengths, as indicated by strength index, are probably at a maximum when the viscosities of the unbleached pulps exceed 1500 cp.

In the case of the birch series, the strength index is adversely affected when the temperature of cooking is 170°C.—the tear increases and the burst and fold decrease.

The maximum strengths of the unbleached pulps, as measured by the strength indices, approach 99 for birch; 85 for poplar; 76 for maple, and 83 for a mixture of 1/3 birch, 1/3 maple, and 1/3 poplar. These strength values probably depend on the natural fiber characteristics of

Table XXVII. Temperature Effects

Max. temp., °C.	Na_2O, %	K No.	Viscosity	Screenings, %	Yield screened pulp, %	Total yield, %
145	18	25.2	3200	8.7	41.8	50.5
150	18	19.2	7260	1.4	51.2	52.6
155	18	15.9	5900	0.6	51.3	51.9
160	18	13.6	1240	0.4	48.6	49.0
165	18	14.8	1030	0.4	48.9	49.3
170	18	11.4	400	0.3	47.4	47.7
175	18	13.2	260	0.3	46.6	46.9

Table XXVIII. Effect of Increasing the Cooking Temperature

No.	Temp., °C.	K No.	Viscosity, cp. (Luke)	Min. to 100 sec. freeness	Luke strength data, total strength values 25, 50, 100, 200 freeness strength				
					Tear	Burst	Break	Fold	Index
				Birch					
41	145	13.1	8375	19	314	252	378	1880	93
43	150	11.1	3825	19	343	270	394	2210	99
46	160	9.3	1292	20	338	272	398	1910	98
51	165	9.5	724	..	...	...	...	...	..
52	170	8.4	414	21	372	218	341	1140	90
				Maple					
59	145	12.7	4032	28	287	176	314	1650	76
63	150	9.8	1923	24	285	160	297	1340	73
68	160	8.3	724	28	276	161	277	1370	71
				Poplar					
69	145	11.5	3833	20	301	186	334	1820	83
71	150	9.3	4343	21	320	195	338	2170	85
73	160	7.3	724	21	304	190	305	1720	80
				Blend of 1/3 Birch, 1/3 Maple, and 1/3 Poplar Chips					
74	145	11.7	3939	20	307	203	335	1500	83
76	150	9.9	3102	20	306	202	304	1180	82
78/9	160	8.3	889	19	284	205	331	1550	81

Table XXIX

Sulphidity	Cooking time hr.	Oven-dry yield, %	K No.	Lignin, %	Alcohol benzol extract, %	Pentosans, %	Viscosity
0	7	48.1	12.9	1.68	0.90	24.7	1000
5.3	5	50.3	12.3	1.32	0.95	26.0	1445
15.0	4	51.6	12.7	1.08	0.99	26.9	2380
25.8	3 1/2	54.8	12.5	1.35	0.72	26.7	4030

the individual woods. It would appear that the three woods can be cooked together under these conditions, and yield a pulp whose strength is equal to a calculated average strength of a blend of the pulps from the woods cooked separately.

The short-fibered unbleached maple stock requires more time to beat to a given slowness than either the birch or poplar.

EFFECT OF SULPHIDITY

Birch chips were cooked with 20% active Na_2O at 160°C. The sulphidity was varied from 0 to 5.3, 15.0, and 25.8%. The cooking time was varied so as to produce pulp of the same K No. The data are shown in Table XXIX.

EFFECT OF BLEACHING

The effect of bleaching sulphate birch pulp is illustrated in Table XXX and of sulphate pine pulp in Table XXXI.

TABLE XXX

Stage	K No.	Viscosity	Brightness
Unbleached	9.2	750	..
(1) Chlorination	...	...	..
(2) Caustic extraction	3.5	517	41
(3) Chlorination	...	...	..
(4) Caustic extraction	2.5	465	54
(5) Hypochlorite	1.2	414	75
(6) Caustic extraction	1.2	362	67
(7) Chlorite	0.8	310	81

Comparison of unbleached and bleached strength values

	Unbleached	Bleached
Beating time, min.	69	68
Tear, total	352	352
Burst, total	211	219
Fold, total	1345	1970
Bulk	5.11	5.02
Strength number	88.6	92.2

Portions of this pulp from the 6th stage were subjected to four special end bleaches. The bleached pulps were then evaluated for strength by the standard Valley beater method. The data are given in Table XXXII.

EFFECT OF FRACTIONATION

When oak pulp at low consistency is flowed over a 40-mesh screen inclined at 45°, the ray fibers go through the openings, whereas the long fibers dewater and roll into clumps off the end of the screen. By this procedure it is possible to separate most of the ray fibers from an oak pulp.

The differences between the whole and long fiber portion of the unbleached pulps and their strength values (TAPPI) are given in Table XXXIII.

DISCUSSION

1. When small chips of hardwood are cooked, a more uniform pulp with a lower K No. is obtained than when large chips are cooked. The strength value of the pulp from the small chips is higher than that of pulp from large chips, particularly in tear.

2. Compression of chips by passage through a mechanical feeder into a continuous digestion apparatus breaks down the physical structure of the chips, and thus makes them more reactive to cooking conditions. However, compression must also have a deleterious effect on the degree of polymerization of the cellulose, because pulp from compressed chips (both before and

TABLE XXXI

Stage	K No.	Viscosity	Brightness
Unbleached	19.8	1400	..
(1) Chlorination	11.0	650	25
(2) Caustic extraction	7.0	830	23
(3) Rue and Sconce	3.0	620	45
(4) Caustic extraction	3.0	720	45
(5) Hypochlorite	1.1	310	68
(6) Caustic extraction	1.0	310	67

[a] Quality index is obtained by mutiplying the brightness value by the strength index.

Table XXXII

End Stage Bleach	Cl_2 %	Conditions: pH	Time, min.	Consumed, %	Temp. °C.	Analysis: 3% NaOH soluble	Viscosity	Brightness
Acid hypochlorite	1.0	6.8	60	2½	65	28.9	26	80
Low density hypochlorite	1.0	9.5	120	2½	40	12.6	248	74
High density hypochlorite	1.0	9.5	120	15	26	14.8	165	73
Chlorine-activated chlorite	2.0	3.6	60	2½	80	13.4	181	85

Strength evaluation of four final pulps

Treatment	Acid hypochlorite	Low density hypochlorite	High density hypochlorite	Chlorine activated chlorite
Beating time	47	80	80	92
Tear, total	314	485	447	504
Burst, total	174	254	244	250
Fold, total	840	2250	2970	2140
Bulk	5.58	5.48	5.64	5.50
Strength index	79.5	110.2	106.9	110.7
Brightness	80	74	73	85
Quality index[a]	64	82	79	95

[a] Quality index is obtained by multiplying the brightness value by the strength index.

after bleaching) is lower in viscosity and strength. The difference in strength is spread equally over the tear, burst, and fold values. The loss in strength from compression is approximately 15%.

3. When the same mixture of coniferous woods is cooked by the acid sulphite and sulphate methods and the pulps evaluated for strength before and after bleaching, the sulphate cooked pulp has a 20% higher strength value, particularly in tear and burst.

4. When the same deciduous wood (birch) is cooked by the sodium sulphite semichemical, full monosulphite, and sulphate method, and then carefully bleached, it is found that (a) the semichemical process gives a 10% higher yield (wood basis) than the other two processes; (b) the semichemical and full monosulphite pulps are easier to bleach than the sulphate pulp; (c) the semichemical and full monosulphite pulps have enough material soluble in hot 3% caustic soda to place it in the category of a good glassine-type pulp; and (d) the sulphate pulp has distinctly higher tear values than the pulps by the other two processes.

5. When an acid chlorite-NaOH is used to pulp acid hydrolyzed and untreated oak chips, the pulp from the untreated chips is much stronger than the pulp from the same oak wood cooked in the mill. The pulp from the acid-hydrolyzed wood has very low tear, tensile, and fold values.

6. When 20% active Na_2O on the wood is used to cook birch chips, there is no significant change in pulp quality when the concentration of the cooking liquor was 20 and 50 g./l. active Na_2O. When the concentration of active Na_2O. When the concentration of active Na_2O was 80 g./l. the unbleached pulp was harder to beat, and had higher tear but lower burst and fold values than the pulps cooked at 20 and 50 g./l. Na_2O.

7. When the percentage and concentration of active Na_2O on the wood was doubled, the two unbleached pulps were quite different in strength properties. The unbleached pulp from the cook at normal concentration was high in viscosity and strength index. The pulp from the cook at high concentration was low in viscosity, difficult to hydrate, and had a high tear value but was deficient in burst and fold.

8. When a mixture of gum and oak wood is cooked by the sulphate process, where the only variable is the maximum temperature reached during the cooking, it is found that as the temperature is increased from 145 to 175°C. in steps of 5°C. pulps of lower K No. and viscosity are produced. The yield of oven-dry screened pulp on the wood basis also drops from 51.3 to 46.6% with the same temperature change. The advantage of low temperature cooking of hardwoods is the high viscosity values of the pulp. With these high viscosity values it is possible to accept the inevitable losses of viscosity which result from bleaching and still have a bleached pulp of high viscosity and strength.

9. When birch wood is cooked by the sulphate process, where the only variable is the sulphidity of the cooking liquor, it is possible to decrease the time of cooking from 7 hours (zero sulphidity) to 3½ hours (25.8%) sulphidity and still obtain pulps in the same K No. range. As the sulphidity is increased from zero to 5.3, 15.0, and 25.8, the yield of unbleached pulp, the pentosan content and the viscosity also increase.

10. The bleaching sequence used to purify and brighten an unbleached coniferous or deciduous pulp controls the strength quality of the final pulp. This is particularly true of warm, high-density oxidative stages. When the stages are properly proportioned as to time, temperature, pH, and amount of chemical, it is possible to obtain pulps which are as strong as the original unbleached pulp.

11. The fractionation of deciduous pulp (such as oak) which is rich in ray fibers, produces a pulp which has a higher tear value, but otherwise its properties are much the same as those of the whole pulp. Since deciduous wood pulps are especially deficient in tear value in the low-freeness range, the increase in tear does not justify the expense of or loss of yield due to fractionation.

Table XXXIII

Unbleach	K No.	Viscosity	Bauer-McNett fractionation: On 20	On 35	On 65	On 150	Through 150
Whole	12.2	4380	1.7	33.8	32.9	9.5	22.1
Long	10.6	4940	3.2	40.9	38.2	10.2	7.5
Bleached	*Brightness*	*Viscosity*	*On 20*	*On 35*	*On 65*	*On 150*	*Through 150*
Whole	70.9	488	3.1	35.7	31.7	8.3	21.2
Long	71.4	802	4.9	43.1	35.8	9.2	7.0

Pulp	Time	Tear	Burst	Fold	Strength Index	Bulk
Unbleached whole	77	419	189	970	87.3	5.54
Bleached whole	81	397	197	950	86.9	5.50
Unbleached fractionated	92	478	205	1060	95.1	5.68
Bleached fractionated	100	467	225	1500	99.7	5.62

	Opacity: 25 Williams	50 Williams	100 Williams	200 Williams
Bleached whole	54.6	52.6	50.2	48.0
Bleached fractionated	52.4	48.8	47.2	45.2

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The data presented in this paper have been culled from a large number of reports prepared by members of the West Virginia Pulp and Paper Co. organization, particularly W. M. Welton, D. B. Westcott, and D. O. Adams.

Comparative Degrees of Preferred Orientation in Nineteen Wood Pulps as Evaluated from X Ray Diffraction Patterns

GEORGE L. CLARK

Continuing the x ray diffraction analysis of wood pulps, and supplementing the five unbleached kraft pulps, 14 additional pulps have been investigated, representing other wood types and the effects of bleaching and processing. The 19 pulps are compared as to the degree of preferred orientation of cellulose chains in the fibers, ranging from unbleached Douglas-fir with very high orientation to some bleached pulps with very nearly random arrangement. The order for the first five pulps is compared with the respective orders for five other measured properties, with a fairly close correlation except for loblolly pine. Qualitative observations are made on crystalline and amorphous phases in these pulps. The work described in this report is to be considered as preliminary in nature. The significance of the results and particularly of the low order of orientation for Mitscherlich pulps is receiving further study.

Recently the author (*1*) presented results of the x ray diffraction analysis of the preferred orientation of cellulose chains for (1) Douglas-fir, (2) black spruce, (3) western hemlock, (4) western red cedar, and (5) loblolly pine. These are listed in the order of decreasing degree of preferred orientation or increasing randomness, from the measurement of the length of the equatorial arc of the 002 interference on the typical cellulose patterns by means of a microphotometer, and calculation of the percentage of cellulose crystallites over each 5° angular range from 0° to 90°.

There are some interesting correlations with other measurable properties of these same pulps as reported in the other papers in the symposium (*2*). For example, the same order as listed above for the orientation is found for decreasing fiber lengths (with the exception of loblolly pine which is second to Douglas-fir in this respect); in other words, the order is 1, 5, 2, 3, 4. Bursting strengths increase and tensile strengths decrease in about the same order; the degree of polymerization decreases in the order 1, 5, 2, 4, 3. Thus, there is a fair correlation, especially for Douglas-fir, between orientation and other properties; loblolly pine shows the greatest discrepancy since, in all cases, it ranked next to Douglas-fir but its x ray patterns displayed the most nearly random distribution of crystallites in comparison with the most highly fibered Douglas-fir. Thus other factors, in addition to fiber texture, must be involved in test data for kraft pulps, as might be expected.

That there are wide variations in cellulose orientation in wood is clearly understood. Bailey and associates (*3*), among others, have shown microscopically for conifers such variations in passing from layer to layer in the secondary walls, and fluctuations within a single layer. Differences in radial, tangential, and transverse sections, spring- and summerwood sections under various pressures and growing variables, and wood subjected to other factors have been demonstrated in x ray patterns in previous papers from the present author's laboratory (*4*) and elsewhere. In a very recent paper Sen and Banerjee (*5*) have shown that cellulose orientation can be changed (usually improved) by enzymatic hydrolysis. Unquestionably bleaching and other chemical treatments must also affect orientation. In view of such variability there has been considerable criticism of most test methods. However, by the method of sample selection and preparation for x ray analysis, a fair average of any given gross specimen is undoubtedly indicated on the patterns.

In view of the interesting results for the five types of conifer pulps already reported, it has seemed desirable to extend the comparative studies of orientation to other types of wood pulp, and to investigate the effects of bleaching and differences in the regular kraft and sulphite process pulps. The same experimental techniques were employed, so that data on 14 new samples may be integrated with those for the first five. Single fibers were teased from each specimen and arranged carefully in parallel bundles as nearly as possible 1 mm. thick. Filtered copper K-alpha radiation was directed perpendicular to the bundle axis and the pattern registered on flat films at a distance of 5 cm., with an exposure time of 45 minutes. The intensity distribution around the strong 002 ring on the cellulose patterns was measured by means of a Gaertner densitometer with a special rotating stage.

In addition to the identification of crystalline cellulose and the evaluation of fiber orientation, the x ray diffraction pattern may also be used to estimate the relative proportions of crystalline and amorphous fractions in a specimen. The first is indicated by the sharp crystalline rings or arcs, and the second by background scattering or fogging of the film. Several published papers on the theory and practice of this method have clearly indicated the relatively greater ratio of amorphous to crystalline phases in wood pulp in comparison with cotton linters, in rayons over natural fibers, and in bleached and in alkaline- or acid-hydrolyzed celluloses in comparison with normal untreated fibers. It does not follow directly that greater randomness in orientation of crystalline cellulose should be accompanied by or eventuate in a higher fraction of amorphous cellulose. This interesting and important point has never been quantitatively studied; but it is undoubtedly true that randomness of orientation is associated with greater penetrability of reagents into a gross specimen, since the cross-linking forces between parallel molecules in highly oriented fibrils are sufficiently strong to resist disorienting tendencies. Thus, it is reasonable that a

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random orientation of crystallites may be antecedent to further molecular disarrangement within crystalline domains into amorphous cellulose which represents the optimum state for swelling, dispersing, and reactivity.

The original five samples and the 14 additional samples (nos. 6–19) subjected to x ray study were as follows:

1. Douglas-fir kraft unbleached
2. Black spruce kraft unbleached
3. Western hemlock kraft unbleached
4. Western red cedar kraft unbleached
5. Loblolly pine kraft unbleached
6. Ponderosa pine kraft unbleached
7. Western white fir kraft unbleached
8. Western hemlock kraft bleached (compare 3)
9. Balsam spruce kraft unbleached
10. Western larch kraft unbleached
11. Jack pine kraft unbleached
12. Jack pine kraft bleached
13. Poplar kraft unbleached
14. Poplar kraft bleached
15. Poplar sulphite unbleached
16. Poplar sulphite bleached
17. Spruce sulphite unbleached (Mitscherlich)
18. Spruce sulphite bleached (Mitscherlich)
19. Spruce sulphite unbleached

Extremely great care in measuring arc lengths on the equator of the 002 ring finally has led to the following order of increasing arc length or decreasing preferred orientation: 1, 7, 9, 2, 6, 10, 3, 4, 11, 12, 14, 15, 5, 17, 13, 8, 19, 16, 18. A few of many observations on this series seem to lead to the following conclusions:

1. Douglas-fir remains outstanding in having the highest degree of preferred orientation in the entire series; with it is grouped white fir, then the two spruces, ponderosa pine, larch, cedar, hemlock, jack pine, poplar (sulphite), loblolly pine, spruce (sulphite, Mitscherlich), and poplar (kraft) in order.

2. Bleaching in general lowers the degree of preferred orientation; the effect is very slight on jack pine (12), but is very large on western hemlock (3, 8); as an apparent exception, bleached poplar kraft is better oriented than unbleached, but the reverse is true for poplar sulphite; the Mitscherlich spruce sulphite is almost entirely random even in unbleached form.

3. Loblolly pine still seems strangely out of order, since several of the bleached forms of other wood pulps outrank it in a higher degree of preferred orientation. Probably several additional independent samples should be examined in those cases in which the single specimen, which gave several consistent x ray patterns with different fiber bundles, is not truly typical of the average pulp. As indicated earlier, the other measured properties of the pulp rank it close to Douglas-fir.

4. The data must be considered as preliminary in nature; much more work will be required before we can say to what extent the orientation determined is an item of chance or is determined by the pulping process employed.

5. Since it is impracticable to plot 19 curves on the same graph, reference may be made again to Fig. 3 of the previous paper (*1*) (reproduced here as Fig. 1) in which the percentage of crystallites over 5° angular ranges is plotted against angle to the fiber axis. Between 1 and 2 of that figure now appear curves for 7 and 9; between 2 and 3 insert 6 and 10; between 4 and 5 insert 11, 12, 14, and 15; and below 5 appear 17, 13, 8, 19, and 18. At the peak values corresponding to parallel alignment to the fiber axis, or 0° to the axis, we find the following order of values for the percentage of the crystallites:

Specimen	*Percentage at 0° from axis*
1	23.5
7	21.4
9	20.0
2	18.2
6	18.0
10	17.6
3	16.6
4	15.1
11	14.6
12	14.1
14	13.2
15	12.9
5	12.4
17	12.2
13	11.0
8	9.9
19	7.5
16	5.1
18	3.8

As the peak lowers, the curve widens until there is an intercept above 0° on the vertical axis indicative of some intensity of the ring at 90° from the fiber axis.

6. With the present patterns exposed primarily for the purpose of measuring orientation, it is not possible to draw certain conclusions as to the ratio of crystalline to amorphous phases. All experimental conditions were maintained constant, but extraordinary technique is required to make safe interpretations of background scattering. Samples 1 to 10 were closely similar in this respect, but samples 11 to 19 showed considerably greater blackening from the center to the innermost

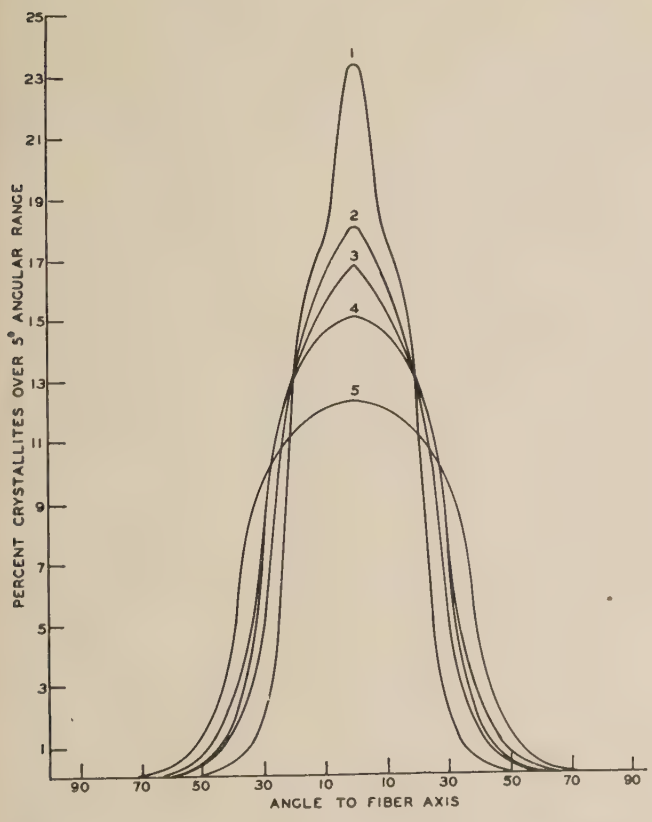

Fig. 1. Preferred orientation in pulp fibers as indicated by the percentage of crystallites over 5° angular ranges as a function of the angle to the fiber axis

[No. 1 (Douglas-fir) is most highly oriented, and No. 5 (loblolly pine) is most nearly random.] (1) Douglas-fir; (2) spruce; (3) hemlock; (4) cedar; and (5) loblolly pine.

rings, which might indicate that jack pine, poplar, and spruce sulphite have a higher amorphous content. If anything, the bleached samples showed less dense blackening along with decreased orientation. Treatment with 0.2% hydrochloric acid at 250°F. markedly changed the pulps to the extent that the background fogging was much diminished as the result of solution of the amorphous phase. Ultimately, it will be of great value to correlate amorphous content as evaluated by x rays and by other methods with absorptive capacity, moisture regain, etc. X ray work will be continued on these same samples with strictly monochromatic x rays, vacuum cameras, and weighed samples in order to evaluate critically the x ray diffraction method for estimating quantitatively the ratio of crystalline to amorphous fractions in various pulps.

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The Proportion of Water-Accessible and Nonaccessible Cellulose in Wood Pulps

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The method of Wink affords a simple and reliable procedure for determining the equilibrium moisture content of wood pulps or other cellulosic materials over a wide range of relative humidity. Absorption moisture regain (after drying over phosphoric anhydride) at 73°F. at intervals between 11.1 and 86.5% relative humidity has been determined for commercial cotton fiber, purified cotton linters, and a series of wood pulps prepared from softwoods and hardwoods by the sulphite, Mitscherlich, and kraft processes; bleached and unbleached pulps were studied. The isotherm derived by Hailwood and Horrobin has been applied to the data as a means of calculating the relative proportions of the material which are accessible and inaccessible to water. The results indicate that wood pulps comprise a class of native cellulosic fibers having a water accessibility which is distinctly higher than that of cotton and much lower than that of mercerized or regenerated cellulose. Different wood pulps show minor variations in accessibility, as do different samples of cotton and cotton linters or different regenerated cellulose samples. In some cases these differences are within the limit of error of the method. The number of samples tested in this work are hardly sufficient to draw any definite conclusions regarding accessibility and different pulping processes or types of pulpwood. The accessibility of poplar pulp appeared to be lower than that of the softwoods. In general the effect of bleaching on the over-all accessibility of the wood pulps to water was not significant. There was an indication that the drying process may have an effect on the accessibility.

For a number of years it has been recognized that the structure of a cellulose system is a mixture of two solid states of aggregation which are interconnected because individual cellulose molecules may extend from one state to the other and thus exist in both states simultaneously. One of these components can be rather clearly defined. It produces an x ray diffraction pattern, indicating that within it the individual molecular chains are arranged in a regular three-dimensional order, like that of a crystal lattice. The other state does not produce an x ray pattern but only a diffuse background in the x ray diagram. Therefore, it has been termed the amorphous portion in distinction to the crystalline portion or crystallite. Unlike the crystalline portion, however, the amorphous regions are not the same throughout, but may vary anywhere from complete randomness to a degree of order just short of complete crystallinity.

Throughout a cellulose sample, therefore, there are conceived to be numerous crystalline areas or crystallites, relatively small in size and interconnected by the same long, threadlike, straight-chain molecules which compose them, but in a less ordered arrangement. The crystalline areas will have the characteristic properties of crystals—that is, greater density and greater tenacity, but low elasticity and flexibility; they are nonreactive and difficult to swell or penetrate with liquids. The amorphous areas, on the other hand, although showing a wide variation from point to point, should be more porous, more flexible, and more easily swollen.

It is of interest, for practical purposes, to know how much of a given cellulose system is in a crystalline state of organization and how much is not. But, largely because of the variation in degree of order of the "amorphous" areas, the results obtained by the different experimental procedures which have been applied to differentiate between the two states have not agreed very well.

At the 1948 meeting of the Fundamental Research Committee of the Technical Association of the Pulp and Paper Industry, Mark (*1*) summarized concisely the different types of experimental methods which have been used for this purpose.

The experimental methods fall into two broad classifications: chemical and physical. The chemical methods aim to distinguish between a rapid rate of reaction in the amorphous regions and a much slower rate in the crystalline regions, and thus to measure the amount of readily reacting or accessible cellulose. Nickerson and

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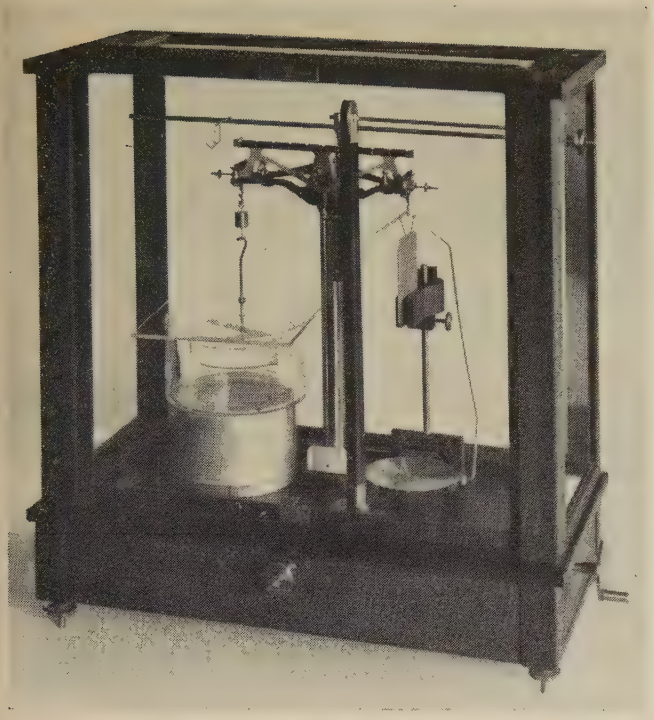

Fig. 1. Glass test unit set up in weighing position

his associates (*2*) introduced an acid hydrolysis reaction for this purpose. The method has been modified and used by several subsequent investigators (*3*). Periodate oxidation (*4*), thallation with thallous ethylate (*5*), and oxidation with chromium trioxide (*6*) have also been used. The chemical methods all indicate lower proportions of amorphous cellulose than the physical methods. Brenner, Frilette, and Mark (*7*) have proposed that, during the chemical reaction in the amorphous regions, the loose chain ends are free to undergo additional recrystallizations so that the degree of crystallinity increases as a consequence of the method of measuring it.

A type of chemical method which avoids the destruction of the sample was utilized by Frilette, Hanle, and Mark (*8*), following an earlier observation of Champetier and Viallard (*9*). The rate of exchange of cellulose with deuterium oxide or heavy water was measured and plotted against the time of reaction. It was observed that the usual initial rapid rate was followed by a nearly constant slow rate and the values for the accessibility of different cellulosic materials obtained by this method are closer to the results obtained by the physical methods.

There are three physical procedures presently available for estimating the percentage of crystalline or well-ordered areas. All three have been examined and used by P. H. Hermans and his associates (*10*). In one, the specific gravity of the sample is measured and, from the calculated values of the specific gravity of the completely crystalline and the completely amorphous cellulose, the percentage of crystalline cellulose is obtained, on the basis that the specific gravity varies directly with the proportions of crystalline and amorphous cellulose.

The second physical method employs the definition of crystalline cellulose as that portion which shows an x ray diffraction pattern. By very careful measurements of the intensity of the interference rings and the diffuse background, Hermans and Weidinger (*11*) have arrived at values for the crystallinity of a number of samples of native and regenerated cellulose. Native fibers are considered to be approximately 70% crystalline, regenerated cellulose (rayon) about 40%. One wood pulp by this method showed 65% crystallinity.

The third physical method involves the measurement of equilibrium moisture content under controlled conditions. The heat of wetting may also be measured. It is assumed, as a first approximation, that native cellulose fibers absorb water in the amorphous portions, but not in the interior of the crystallites and that, accordingly, there will be a correlation between the moisture regain and the proportion of accessible or swellable cellulose in the sample.

Howsmon (*12*) has measured the moisture sorption at 58 ± 1% relative humidity and 75 ± 1°F. of oven-dried samples and obtained accessibility values relative to that of cotton. One wood pulp sample (not otherwise identified) was included. Its sorption ratio as compared with cotton was 1.20.

The experimental procedure is the simplest of the physical methods and the present paper contains the results which have been obtained in our Cellulose Laboratory on a number of different wood pulp samples.

EXPERIMENTAL

In order to obtain absorption moisture data, the samples were suspended in closed vessels in atmospheres of fixed relative humidity, these being controlled by saturated salt solutions in the bottom of the container. The tests were carried out in a room in which the temperature was maintained at 73°F. Each sample was placed in an open-glass Petri dish suspended in a covered crystallizing dish by means of a brass rod which passed through a hole in the cover, and terminated in a hook. A conical collar soldered on the rod fitted into a tapered hole in the cover and effectively sealed the opening. By hooking the end of the rod onto one arm of an analytical balance, the Petri dish and the sample hung freely and could be weighed without altering the conditions of relative humidity. The general principle of the method was

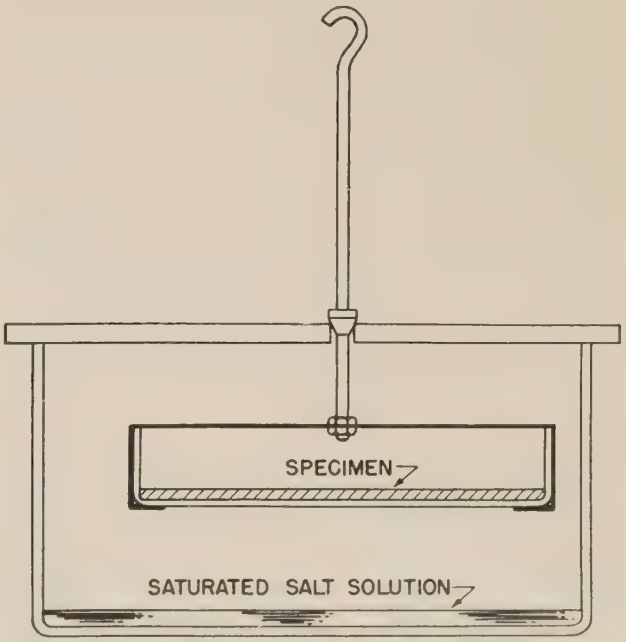

Fig. 2. Schematic diagram of the glass test unit

Table I. Water-Accessible Portion of Cellulose Materials Calculated from Absorption Moisture Regain

Sample[a]	M	α	β	$\alpha\beta$	Inaccessible, %	Accessible, %	Inaccessible accessible ratio
Cotton linters	474.2	0.00772	7.05	0.0544	65.8	34.2	1.92
Cotton fiber	439.0	0.00753	9.40	0.0708	63.1	36.9	1.71
Unbleached Kraft Pulps							
Douglas-fir	349.8	0.00772	11.02	0.0851	53.7	46.3	1.16
Loblolly pine	321.6	0.00739	9.61	0.0710	49.6	50.4	1.02
Western hemlock	332.2	0.00748	10.34	0.0773	51.1	48.8	1.05
Laboratory Single-Stage Calcium Hypochlorite Bleach of Douglas-Fir							
Unbleached	344.8	0.00752	9.77	0.0735	53.0	47.0	1.13
Bleached	334.7	0.00704	11.42	0.0803	51.6	48.4	1.07

[a] Cotton and cotton linters in bulk. Pulp samples as handsheets.

proposed by Gane (*13*), but the equipment and experimental procedure used were developed by Wink (*14*), and have been described by him in detail. Figures 1 and 2 show the test unit and the arrangement for the weighing operation.

To carry out a test, the balance was adjusted to zero position with a counterpoise of suitable weight in place of the left hand balance pan. The balance was subsequently zeroed to this counterpoise weight each time before the samples were weighed. For each sample, the weight of the empty Petri dish and suspending apparatus was first determined, after which pieces of the sample (about half a gram) were distributed over the bottom of the Petri dish. Since all moisture values were obtained on an absorption cycle, the sample was first placed over phosphoric anhydride to dry it as completely as possible under these conditions. It is recognized that some moisture undoubtedly remained in the material. Weighings were made at approximately 24-hour intervals until the weight became constant. The sample (including Petri dish, suspending device, and cover) was then placed over the saturated salt solution giving the lowest relative humidity of the selected series, and the weighings were repeated until equilibrium was reached. It was then transferred to the next higher relative humidity condition, and so on. After the series was finished, the sample was again dried over phosphoric anhydride, as a check. The moisture content at each condition of relative humidity was calculated as a percentage of the phosphoric anhydride dry weight of the sample.

The saturated salt solutions given below were used.

	Relative humidity at 73°F., %
Lithium chloride	11.1
Potassium acetate	22.9
Magnesium chloride	32.9
Potassium nitrate	48.6
Sodium nitrate	64.8
Sodium chloride	75.5
Potassium chromate	86.5

In most cases, the moisture absorptions were determined on duplicate samples as shown in Tables IV, V, and VI.

Table II. Comparison of Douglas-Fir Kraft Pulps from Springwood and Summerwood

	M	α	β	$\alpha\beta$	Inaccessible, %	Accessible, %	Inaccessible accessible ratio
A. In bulk, as received							
Springwood	332.5	0.00756	9.95	0.0753	51.3	48.7	1.05
Summerwood	342.0	0.00732	8.18	0.0599	52.6	47.4	1.11
B. Heat-dried handsheets							
Springwood	335.6	0.00754	10.15	0.0765	51.7	48.3	1.07
Summerwood	344.4	0.00737	10.15	0.0748	53.0	47.0	1.15
C. Air-dried handsheets							
Springwood	311.8	0.00743	9.88	0.0734	48.0	52.0	0.92
Summerwood	318.4	0.00724	9.03	0.0654	49.1	50.9	0.96

Calculation of the Nonaccessible to Accessible Cellulose Ratio

The isotherm derived by Hailwood and Horrobin

Table III. Water-Accessible Portion of Commercial Wood Pulps Calculated from Absorption Moisture Regain

Sample	M	α	β	$\alpha\beta$	Inaccessible, %	Accessible, %	Inaccessible accessible ratio
Unbleached spruce sulphite	347.6	0.00744	11.03	0.0821	53.4	46.6	1.15
Unbleached spruce Mitscherlich	353.2	0.00799	9.54	0.0762	54.1	45.9	1.18
Bleached spruce Mitscherlich	353.0	0.00772	10.17	0.0785	54.1	45.9	1.18
Unbleached jack pine kraft	332.8	0.00770	9.60	0.0739	51.3	48.7	1.05
Bleached jack pine kraft	363.5	0.00779	9.37	0.0730	55.4	44.6	1.24
Unbleached poplar sulphite	362.2	0.00774	9.81	0.0759	55.3	44.7	1.24
Bleached poplar sulphite	355.5	0.00767	10.45	0.0801	54.4	45.6	1.19
Unbleached poplar kraft	374.4	0.00778	9.95	0.0774	56.7	43.3	1.31
Bleached poplar kraft	381.0	0.00775	13.27	0.1028	57.5	42.5	1.35

Table IV. Moisture Regain of Pulp at 73°F.

(As Grams of Water per 100 Grams of Phosphoric Anhydride-Dried Sample)

Sample	Percentage relative humidity moisture regain					
	11.1	22.9	32.9	48.6	64.8	75.5
Cotton linters						
1	1.8	..	3.7	5.0	6.8	8.3
2	1.8	..	3.7	5.1	6.85	8.3
Av.	1.8	..	3.7	5.1	6.8	8.3
Calcd.	1.79	..	3.72	5.06	6.75	8.35
Cotton fiber						
1	2.2	3.35	4.2	5.65	7.4	8.9
2	2.15	3.45	4.15	5.55	7.25	8.7
Av.	2.2	3.4	4.2	5.6	7.3	8.8
Calcd.	2.18	3.39	4.22	5.54	7.27	8.86
Unbleached Kraft Pulps						
Douglas-fir						
1	2.8	..	5.45	7.2	9.45	11.55
2	3.2	4.5	5.50	7.5	9.8	11.75
Av.	3.0	..	5.5	7.35	9.6	11.65
Calcd.	2.98	4.51	5.54	7.25	9.51	11.65
Loblolly pine						
1	2.9	..	5.7	7.3	9.7	11.65
2	3.1	4.5	5.7	7.5	9.9	11.85
Av.	3.0	..	5.7	7.4	9.8	11.75
Calcd.	2.97	4.61	5.72	7.47	9.75	11.77
Western hemlock	3.05	..	5.6	7.3	9.7	11.55
Calcd.	2.99	..	5.66	7.39	9.63	11.68
Laboratory Single-Stage Calcium Hypochlorite Bleach of Douglas-Fir						
Unbleached	2.85	..	5.4	7.05	9.3	11.25
Calcd.	2.81	..	5.40	7.07	9.28	11.26
Bleached	3.0	..	5.5	7.05	9.1	10.75
Calcd.	2.97	..	5.51	7.08	9.02	10.72

(*15*), in the reduced form assuming the formation of a monohydrate only, has been applied to the data obtained here. In their model it is assumed that the absorbed water exists in two states: first, as water in simple solution and, second, as water combined to form a hydrate with a definite unit of the polymer; and that the three species in the solid phase—dissolved water, hydrated and unhydrated polymer molecules—form an ideal solid solution.

For a monohydrate, the equation has the form:

$$\frac{Mr}{1800} = \frac{\alpha h}{1 - \alpha h} + \frac{\alpha\beta\, h}{1 + \alpha\beta\, h},$$

in which M is the "molecular weight" of the operative polymer unit, r is the moisture regain in grams per 100 grams of dry sample, h is the percentage relative humidity, and α and β are constants.

Following the suggestion of Hailwood and Horrobin, the equation was converted to the form $A + Bh - Ch^2 = h/r$ for determination of the constants α and β. Data were obtained at five or six relative humidities, but only four points were used in calculating the constants. The moisture regain at 75.5 and 32.9% relative humidity and at 64.8 and 11.1% relative humidity resulted in a value for C which, by substitution, gave two figures for B, and four figures for A. M, α, and β could then be evaluated.

The inaccessible or nonswellable fraction of the cellulosic material (molecular weight of the glucose anhydride structural unit = 162) was given by $(M - 162)/M$.

In this derivation, the formation of a monohydrate by the basic glucose anhydride unit has been assumed; this suffices to give good agreement with the experimental moisture regain values between 11.1 and 86.5% relative humidity. Hermans and Weidinger

Table V. Moisture Regain at 73°F. of Kraft Pulps from Douglas-Fir Springwood and Summerwood

(As Grams of Water Per 100 Grams of Phosphoric Anhydride-Dried Sample)

Sample	Percentage relative humidity moisture regain				
	11.1	32.9	48.6	64.8	75.5
A. In bulk, as received					
Springwood					
1	3.0	5.70	7.4	9.8	11.95
2	2.95	5.60	7.4	9.6	11.6
Av.	3.0	5.65	7.4	9.7	11.8
Calcd.	2.97	5.66	7.39	9.69	11.81
Summerwood					
1	2.6	5.1	6.85	9.05	10.7
2	2.65	5.1	6.9	8.95	10.75
Av.	2.6	5.1	6.9	9.0	10.7
Calcd.	2.56	5.16	6.83	8.92	10.82
B. Heat-dried handsheets					
Springwood					
1	2.95	5.6	7.3	9.55	11.5
2	3.0	5.6	7.3	9.6	11.65
Av.	3.0	5.6	7.3	9.6	11.6
Calcd.	2.95	5.61	7.33	9.59	11.66
Summerwood					
1	2.9	5.5	7.15	9.3	11.1
2	2.8	5.3	6.9	9.1	10.9
Av.	2.85	5.4	7.0	9.2	11.0
Calcd.	2.84	5.39	7.02	9.11	10.99
C. Air-dried handsheets					
Springwood					
1	3.1	5.75	7.7	10.1	12.25
2	3.2	6.00	7.9	10.1	12.3
Av.	3.15	5.9	7.8	10.1	12.3
Calcd.	3.11	5.94	7.77	10.12	12.27
Summerwood					
1	2.9	5.5	7.3	9.5	11.6
2	2.95	5.7	7.5	9.7	11.6
Av.	2.9	5.6	7.4	9.6	11.6
Calcd.	2.88	5.61	7.37	9.56	11.53

(*16*) have postulated the existence of two hydrates of cellulose with the basic formulas: $C_6H_{10}O_5 \cdot 1/3\ H_2O$ or $C_6H_{10}O_5 \cdot 1/2\ H_2O$ and $C_6H_{10}O_5 \cdot 1^1/_3\ H_2O$ or $C_6H_{10}O_5 \cdot 1^1/_2\ H_2O$ which, substituted in the isotherm of Hailwood and Horrobin, might give values even closer to the experimental results, but would considerably complicate the mathematical computations.

RESULTS AND DISCUSSION

The samples included in this work were obtained at different times and have been divided into three general groups. The first, which appears in Tables I, IV, and VII, included a cotton fiber, a commercial purified cotton linter, and handsheets of kraft pulps from three softwoods: Douglas-fir, western hemlock, and loblolly pine. All these pulps were unbleached, but a single-stage calcium hypochlorite bleach of the Douglas-fir pulp resulted in a General Electric brightness of 81.1.

As expected, the wood pulps are in a separate class from cotton linters and cotton fiber as regards moisture absorption and accessibility. It will be noted, however, that there was a definite difference between the long fiber cotton and the purified cotton linters, the latter having a lower moisture regain at all relative humidities. The ratio of inaccessible to accessible cellulose in this material agrees fairly well with the results obtained by other investigators using physical methods. The accessibility of wood pulp, as compared with cotton linters, is also in line with results previously published.

Of the three wood pulps, loblolly pine shows the greatest accessibility and Douglas-fir the least. Bleaching caused a small increase in accessibility. It will be seen in Table VII that, from the Hailwood and Horrobin isotherm, the amount of bound hydrate water increased on bleaching, whereas the amount of free dissolved water decreased.

The second group of samples, with the data summarized in Tables II, V, and VII, were concerned with a mechanical separation of Douglas-fir pulpwood into its springwood and summerwood constitutents. They

Table VI. Moisture Regains at 73°F. of Commercial Wood Pulps

(As Grams of Water per 100 Grams of Phosphoric Anhydride-Dried Sample)

Sample	*Percentage relative humidity moisture regain*					
	11.1	*32.9*	*48.6*	*64.8*	*75.5*	*86.5*
Unbleached spruce sulphite						
1	2.95	5.53	7.10	9.24	11.05	14.80
2	2.94	5.38	7.03	9.08	11.02	14.70
Av.	2.95	5.45	7.1	9.2	11.0	14.75
Calcd.	2.94	5.46	7.08	9.18	11.07	13.87
Unbleached spruce Mitscherlich						
1	2.98	5.46	7.35	9.91	12.22	16.10
2	2.89	5.35	7.27	9.60	11.58	15.21
Av.	2.9	5.4	7.3	9.75	11.9	15.65
Calcd.	2.84	5.45	7.24	9.69	12.07	15.73
Bleached spruce Mitscherlich						
1	2.78	5.35	7.08	9.36	11.47	14.82
2	2.93	5.43	7.28	9.46	11.45	15.05
Av.	2.85	5.4	7.2	9.4	11.5	14.9
Calcd.	2.85	5.41	7.09	9.36	11.47	14.72
Unbleached jack pine kraft						
1	3.02	5.62	7.51	9.94	12.07	15.41
2	2.98	5.64	7.50	9.96	11.96	15.89
Av.	3.0	5.6	7.5	9.95	12.0	15.65
Calcd.	2.94	5.66	7.45	9.85	12.14	15.41
Bleached jack pine kraft						
1	2.81	5.32	6.97	9.17	11.20	14.75
2	2.57	5.16	6.91	9.09	11.10	14.37
Av.	2.7	5.2	6.9	9.1	11.15	14.56
Calcd.	2.69	5.21	6.89	9.14	11.27	14.49
Unbleached poplar sulphite						
1	2.77	5.14	6.90	9.26	11.14	14.25
2	2.81	5.34	7.05	9.08	11.09	14.47
Av.	2.8	5.2	7.0	9.2	11.1	14.35
Calcd.	2.74	5.25	6.89	9.15	11.18	14.46
Bleached poplar sulphite						
1	2.80	5.33	6.95	9.15	11.25	13.84
2	2.92	5.42	7.08	9.26	11.34	14.91
Av.	2.85	5.4	7.0	9.2	11.3	14.4
Calcd.	2.86	5.37	7.04	9.27	11.31	14.31
Unbleached poplar kraft						
1	2.68	5.12	6.74	8.89	10.91	13.86
2	2.65	5.13	6.68	8.89	10.83	14.12
Av.	2.7	5.1	6.7	8.9	10.9	14.0
Calcd.	2.67	5.10	6.73	8.90	10.92	14.08
Bleached poplar kraft						
1	3.02	5.31	6.78	9.04	10.98	14.26
2	3.04	5.19	6.67	8.92	10.84	14.08
Av.	3.0	5.25	6.7	9.0	10.9	14.2
Calcd.	2.97	5.25	6.80	8.85	10.83	13.82

were then pulped separately by a kraft process. One set of determinations was made on the pulp as it was received; another set was made on handsheets dried in the usual way against a steam-heated metal surface, and a third set on handsheets which were allowed to dry at room temperature. In all cases, the springwood was a little more accessible to water than the summerwood. The results with bulk pulp and ordinary handsheets checked, but the air-dried handsheets, both springwood and summerwood, were considerably more accessible. This suggests that secondary valence bonds may be formed in the amorphous portions of the cellulose on drying which decrease the accessibility of the material to water.

The third group of samples was tested most recently; the data are presented in Tables III, VI, and VII. An attempt was made to include hardwoods and softwoods pulped by acid and alkaline processes; unbleached and bleached samples were studied. As nearly as possible, the bleached pulp came from the same source as the unbleached. Unfortunately, a sample of bleached spruce sulphite corresponding to the unbleached sample could not be secured.

The difference in water accessibility is not great in this group of pulps. However, a more extensive study would have to be made to have an adequate basis for conclusions as to differences in woods.

The poplar pulps have the highest inaccessible-accessible cellulose ratio.

In most cases bleaching had only a very minor effect on the proportion of accessible material as measured by

Table VII. Calculated Moisture Regain at 100% Relative Humidity and 73°F.

(Grams per 100 Grams Phosphoric Anhydride-Dried Sample)

Sample	*Total water*	*Free dissolved water*	*Hydrate water*	*Hydrate water, accessible fraction*
Cotton linters	16.08	12.87	3.21	9.40
Cotton fiber	16.14	12.55	3.59	9.73
Kraft pulps				
Unbleached Douglas-fir	22.15	17.55	4.60	9.93
Unbleached loblolly pine	20.63	15.72	4.91	9.75
Unbleached western hemlock	20.89	16.09	4.80	9.84
Unbleached Douglas-fir	20.59	16.00	4.59	9.77
Bleached Douglas-fir	17.57	12.79	4.78	9.88
Douglas-fir springwood				
In bulk	21.58	16.80	4.78	9.81
Heat-dried handsheet	21.18	16.43	4.75	9.84
Air-dried handsheet	21.78	16.70	5.08	9.78
Douglas-fir summerwood				
In bulk	18.89	14.38	4.51	9.52
Heat-dried handsheet	19.26	14.65	4.61	9.80
Air-dried handsheet	19.74	14.84	4.90	9.63
Unbleached spruce sulphite	19.80	15.18	4.62	9.91
Unbleached spruce Mitscherlich	25.00	20.49	4.51	9.83
Bleached spruce Mitscherlich	21.68	17.16	4.52	9.85
Unbleached jack pine kraft	22.88	18.12	4.76	9.78
Bleached jack pine kraft	21.67	17.31	4.36	9.78
Unbleached poplar sulphite	21.59	17.20	4.39	9.81
Bleached poplar sulphite	21.17	16.67	4.50	9.87
Unbleached poplar kraft	21.17	16.91	4.26	9.85
Bleached poplar kraft	20.45	16.15	4.30	10.11

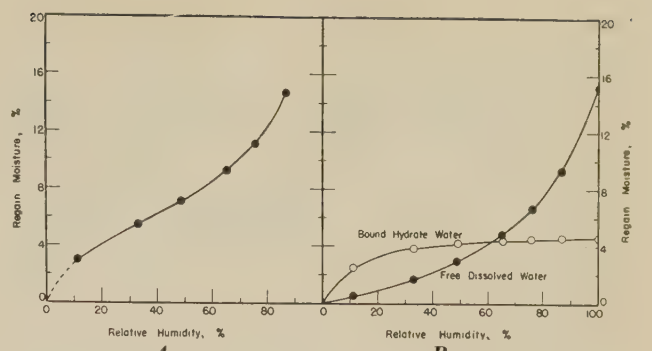

Fig. 3. A. Absorption moisture regain isotherm of unbleached spruce sulphite wood pulp at 73° F. B. Absorption moisture regain of unbleached spruce sulphite pulp calculated from the isotherm of Hailwood and Horrobin. •—Free dissolved water; ○—Bound hydrate water.

water sorption. Although the free dissolved water, as calculated by the Hailwood and Horrobin isotherm, was consistently lower after bleaching, the bound hydrate water tended to increase. An exception was jack pine (a softwood) when pulped by the kraft process, which showed a distinct decrease in accessibility on bleaching.

The Hailwood and Horrobin isotherm gave good agreement with the experimental data. Typical curves are shown in Figs. 3-A and 3-B for one sample—unbleached spruce sulphite pulp. In Table VII the isotherm has been used to calculate the water contents to be expected at 100% relative humidity for all the samples; this moisture is divided into the free dissolved water and the hydrate or adsorbed water components. In the last column in Table VII this hydrate water regain is divided by the accessible fraction of cellulose in the sample, giving a fairly constant value for all the materials tested.

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The Role of Pulp Viscosity and the Degree of Polymerization in Papermaking

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The average degree of polymerization of a pulp (related to the average molecular weight of the carbohydrate fraction) may be determined by a number of methods. Of these, the viscosity of a pulp solution in cuprammonium or cupriethylenediamine is most commonly used. The viscosity determination is of value in the control of loss of pulp quality during processing or as a specification in the manufacture or purchase of a pulp for a definite use. The standard methods currently approved are time consuming and rather tedious. Quick methods are needed for control, and the cupriethylenediamine method of Straus and Levy seems to fit the requirement. Some modification of this should be worked out and accepted as a standard method. Fractional solution methods for determining the chain length distribution in a nitrated pulp are inadequate and misleading. Fractional precipitation of a nitrated pulp from acetone solution by water has been refined to the point of real utility. Further studies of the type of Tasman and Corey and of Jörgensen should provide information of significance.

THE cellulose fiber is a complex structure—a product of a biological process involving first the deposition of a cambial or primary wall, and then a secondary wall of various zones and lamella, with a considerable variation in the chemical make-up between and within walls, zones, and lamella. It is one phase of this complex material which we wish to discuss at the present time—the molecular weight relationships of the carbohydrate material in the fiber.

This morning we have been considering some of the properties of the individual fiber which are related to papermaking. We have heard about the effects of variation in gross size and shape, and have looked into the possibilities that the degree of orientation of the crystallites and the relative amounts of crystalline cellulose may participate as integral components in the summative fiber and sheet properties. We should now like to present some of the developments which have come from a consideration of the part played by the average length or degree of polymerization of the cellulose chain.

By chain length or degree of polymerization (D.P.), we mean the number of anhydroglucose residues which are linked together to form the particular cellulose molecule. The number of such glucose units in the enormous number of cellulose molecules making up the fiber will of course vary over a considerable range. The average molecular weight or degree of polymerization will represent the average value for all the molecules in the sample. Such a value has fairly wide application, but only limited significance. Of greater interest, particularly to the user of pulp for chemical conversion, is the distribution of these various chain lengths into a number of fractions of increasing average degree of polymerization or chain length. Here we break up the one average D.P. value of the sample into any number of average D.P. values for a series of samples. The estimation of the actual molecular distribution by D.P.'s is still a goal some distance in advance of us. Two pulps may have the same average D.P. but exhibit a great difference in distribution on fractionation; such pulps will exhibit very different papermaking properties, other conditions being equal.

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METHODS FOR ESTIMATING THE AVERAGE D.P. OF A PULP

The methods which have been used for estimating the average D.P. of a pulp may be classified either as chemical methods or as physical methods.

The chemical methods are based upon some chemical property of the chain molecule. As an illustration, there is the end-group determination which involves a measure of the reducing activity of the potential aldehyde group in the end glucose unit. From the amount of reduced cupric copper formed when Fehling solution is used, the number of reducing groups per gram of cellulose can be calculated. Other end-group methods of this type depend upon the use of iodine or the reaction between ethyl mercaptan and the reducing group. Still another chemical end-group method is that which is based upon the difference in the number of hydroxyl groups in one of the end glucose units as compared with the other glucose units in the chain. When cellulose is completely methylated by an appropriate reagent and the fully methylated cellulose is hydrolyzed, we obtain a mixture of tri- and tetramethylglucoses. This mixture is separated by distillation *in vacuo*. The tetramethylglucose, isolated from the end glucose unit, is purified and weighed. The yield of this gives us a means for calculating the average molecular weight.

The other general method for determining the average molecular weight or average degree of polymerization of cellulose, is that involving the use of physical methods. Here we can apply the usual procedures for determining molecular weight, such as a measurement of osmotic pressure or viscosity or, finally, the methods using the ultracentrifuge. Because of the limited solubility of cellulose itself, the osmotic pressure method has to be used with cellulose derivatives. It is the feeling of Heuser (*1*) that difficulties involved in the use of the osmotic pressure method have been largely overcome and that the modified methods thus developed should yield fairly reliable results. The second method, based upon a measurement of the viscosity of a cellulose solution, has been very widely used. The principal solvents employed for dissolving the cellulose samples are cuprammonium hydroxide or cupriethylenediamine. Staudinger has developed a constant to establish the

relationship between the viscosity of these solutions and the degree of polymerization of the dissolved material. There are a number of difficulties involved in the determination of the D.P. from the cellulose solution viscosities. Heuser (*2*) has discussed the problem in some detail. Possibly a more effective means for determining molecular weight results when the pulp is nitrated under carefully controlled conditions and the viscosity or osmotic pressure of the nitrated pulp is measured in acetone solution.

The ultracentrifuge method involves the determination of particle size by observing the rate of sedimentation and diffusion. This method is the result of the work carried out by Svedberg; for its application we are indebted to Kraemer, Stamm, and others. Although the equipment is expensive and the procedure rather cumbersome, it seems probable that the ultracentrifuge method may be regarded as the only absolute method of molecular weight determination which is a correct average value.

Workers in the field of pulp and paper have concentrated their activities largely on the viscosity methods, using first cuprammonium hydroxide and, more recently, cupriethylenediamine. The methods as set up determine, of course, the actual viscosity in centipoises of a solution of definite concentration and at constant temperature; for practical purposes this value is never converted into molecular weight.

Bialkowsky (*3*) in 1930, using a modified Shirley Institute method, suggested the cuprammonium viscosity test as a method for following the potential loss of strength of a rag stock during processing. In his report, he showed the loss of viscosity during cooking of rags and the bleaching of the rag stock and gave evidence to support the belief that beating does not result in a loss in viscosity. He also showed the change both in viscosity and in the folding test with an increase in the severity of bleaching conditions. Soon after Bialkowsky's paper was published, other papers appeared relating the viscosity to the more common strength tests such as burst, fold, and the like, following changes in cooking and in bleaching. Among early investigations are those of Parsons (*4*), Ross, Mitchell, and Yorsten (*5*), and Coster (*6*).

One of the problems which needs to be resolved is that of the standardization of a common and, if possible, a rapid method for the determination of the disperse viscosity of a cellulose solution. The majority of the work already described has been carried out by a method from which developed TAPPI Standard T 206, with a 1% cuprammonium solution of the pulp in a standard equipment under controlled conditions. It so happens that the standard method of the American Chemical Society recommends a somewhat different set of conditions. In the first method, a capillary flow viscometer is used, in the second a falling sphere. To add to the confusion, a number of companies have developed their own rapid methods and there is now under serious consideration the substitution of cupriethylenediamine for cuprammonium because of the advantages of the latter in the matter of speed of test and stability and easy availability of the solvent. An ordinary pulp will give a 1% solution in cupriethylenediamine in less than half an hour, and those of very high viscosities will require not more than 1 hour.

The basic methods for viscosity estimation are of particular application for well-cooked unbleached or bleached pulps. Coppick (*7*) has shown that the values for very raw pulps are open to considerable question—here the noncellulosic encrustants interfere with the solution of the carbohydrate material. For the determination of the degree of polymerization of the carbohydrate fraction of finely divided wood or of highly lignified pulps, Coppick recommends the estimation of the viscosity of nitrated pulps in acetone-alcohol-benzene. There is little agreement between the nitric acid method and the use of basic solvents with highly lignified pulps but better agreement is obtained with the basic methods as delignification proceeds—Coppick gives the average D.P. of the wood carbohydrate of aspen as being about 1400, while the value for the white pine carbohydrate fraction is about 1600.

In addition to following the rates of degradation and controlling a given process, the viscosity may be used for specifications of particular types of pulps for specific types of paper. The following discussion relates to such an application. In this case, the method of Straus and Levy (*8*) involving the use of cupriethylenediamine has been used, since the entire test can be run in about 20 minutes with a reproducibility of 1% or better. When the degree of polymerization of a pulp, as gaged by this method, corresponds to a solution viscosity of around 30 cp. (TAPPI 80 cp.) or higher (concentration of dissolved cellulose 0.5%), the fibers tend to shorten relatively slowly and fibrillation can be extensively developed in the ordinary beater. At degrees of polymerization corresponding to a viscosity of about 4 cp. (TAPPI 9 cp.), the fiber is so easily cut or broken that relatively little fibrillation occurs unless the beater-roll pressure is maintained light throughout the beating. At intermediate degrees of polymerization, the pulp fibrillates in an intermediate manner. A viscosity of 30 cp. in the test indicated corresponds to a degree of polymerization of about 1500; a viscosity of 4 cp. to about 600 (*8*).

A good example of the importance of polymerization control in the conditioning of fiber for conversion into a specific type of paper is the manufacture of filter paper. If a sheet is desired which is capable of retaining fine precipitates and which has a moderately high filtering speed, cotton fibers of a high degree of polymerization are preferable, corresponding to a solution viscosity of about 30 cp. If, however, the filter paper is to be of more open structure—i.e., if it is to be used to filter coarser precipitates and is to have maximum speed—the cotton fibers are preferably conditioned to a lower degree of polymerization, corresponding to a viscosity of about 8 cp. (TAPPI 20 cp.). In the first instance, the fibers resist cutting so that, by the time they are reduced to the length needed for good formation on the papermaking machine, they are sufficiently well fibrillated to yield a sheet of uniform, close formation, free from pin holes, yet of relatively good porosity. In the second case, the fibers cut and break more easily, so that by the time they are reduced to the desired fiber length, they have been fibrillated to a lesser extent and, as a result, they yield a sheet of more open structure.

Another significant example is the manufacture of very light carbonizing paper as contrasted with book paper. Carbonizing paper is best made from pulp of

intermediate viscosity, since the fibers must be moderately well fibrillated to yield a thin tissue of uniform structure, free from pin holes, yet reasonably free from cockle and curl; the manufacture of book paper, on the other hand, is facilitated if the pulp is of low viscosity because the fibers, when shortened to the optimum extent, should show only slight fibrillation so that shrinkage of the web on the driers will be relatively low, and the resulting paper will be soft, bulky, and opaque.

Another interesting example is the manufacture of condenser paper which must be well formed, dense, and free from pin holes. The production of this type of sheet is favored when the pulp, usually a thoroughly washed kraft pulp prepared from coniferous wood, has a solution viscosity of at least about 12 cp. (TAPPI 30 cp.). Such pulp permits a proper balance of fibrillation and shortening of the fibers in the beater. In the manufacture of condenser paper of high quality the time required in a typical beater provided with a single bedplate is about 40 hours when the condenser paper is to have a thickness of 0.0003 inch, and about 18 to 20 hours in the manufacture of condenser paper 0.0005 inch thick. If the viscosity of different batches of the pulp varies, the mill has the greatest difficulty in maintaining uniformity both in the handling of the beaters and in the quality of the paper.

In the manufacture of currency paper, a high degree of polymerization is considered to be a necessity, since the flax and cotton components must be fibrillated to an exceedingly great extent in order that the paper may have the necessary toughness and wearing qualities. It is usually preferred that both components of the furnish have a solution viscosity of at least about 30 cp. (TAPPI 80 cp.). The high degree of polymerization also insures maximum tensile strength of the individual fibers and fibrils, and high folding endurance in the final sheet of paper.

These examples might be multiplied many times, but enough has been said to emphasize the importance of the degree of polymerization in papermaking.

It can be seen at once that, for smooth operation of the beater room and of the paper machine, the degree of polymerization of the pulp is worthy of considerable attention. Unless the viscosity of the pulp is maintained substantially constant, beater operation may require constant vigilance, and variations in slowness, average fiber length, and degree of fibrillation of the beater stock are very likely to be reflected in a variable behavior of the fibers on the paper machine and in a variable quality of the finished sheet. Conversely, for most uniform behavior of the pulp in the paper mill and for most uniform quality of paper, the control of the degree of polymerization in the manufacture of most papers of high quality is of extreme importance.

It is natural to inquire why a lowering in viscosity should interfere with the fibrillating properties of pulp. The answer is probably to be found in the drop in tensile strength that normally accompanies a lowering of the degree of polymerization—i.e., "degradation" of the cellulose. Much has been written about the tendering effect of acid and of oxidants on cellulose fibers. When the fibers are pounded or pulled between the beater roll and the bedplate, the lower tensile strength of the degraded fibers manifests itself in rapid shortening. The fibers break before they bruise. The shorter fibers or the fiber fragments do not readily form fibrages, and they consequently tend to escape further pounding or mashing necessary for the development of fibrillation.

It would be interesting and informative to compare the fibrillating properties of various types of cellulose fibers at different levels of viscosity when the fibers are worked in water under conditions that eliminate or greatly reduce the disturbing factors of cutting and fibrage formation. As a step in this direction, the suggestion is made that pulps be vigorously agitated in water in partly filled cylindrical pots—e.g., ball mill pots—mounted at an angle of about 45° to the axis of rotation. The comparative rates of fibrillation under standardized conditions of revolutions per minute, pulp concentration, temperature, etc., would be followed by examination of the pulp at noted time intervals under the microscope, by drainage measurements, by the study of the shrinkage in area of test sheets made and air dried under standardized conditions, and by measurements of porosity and various strength characteristics, including folding endurance, of dry test sheets. The silvering technique of Clark as discussed later on in this program might be used to good advantage to determine the external specific surface of the pulp samples taken at different stages of the run.

It will also be found possible and informative to separate fibrils loosened from fibers by washing the slushed or beaten pulps in a muslin bag with large volumes of water, the meshes of the cloth being kept open by frequent scraping with the hand. The loosened fibrils will pass through the bag and can be separated from the bulk of the wash water by decantation—they then can be made up into test sheets on silk stretched over a wire screen.

Although the beating characteristics of pulp are related to the degree of polymerization, it is well known that other factors must be considered in the selection or preparation of pulps for specific or special uses. Thus, at a solution viscosity of 10 cp. (TAPPI 25 cp.), various types of pulp may have widely dissimilar beating characteristics, even when compared at about the same average initial fiber length. By way of example, cotton and flax fibers, precut dry to an average length of 3 mm., then cooked with caustic soda, carefully bleached to a viscosity of 10 cp., beat quite differently from one another and from bleached spruce soda pulp of about the same initial fiber length. Similarly, bleached spruce sulphite pulp and bleached sulphite pulp of similar viscosity behave quite differently in the beater. If these pulps are dried before they are beaten, their beating properties, as is well known, are drastically altered, even though the viscosity may be substantially unchanged when the pulps are dried. Again, when wood pulp is highly purified to an alpha-cellulose content of over 99%, it fails to respond to beating, although the viscosity may be fairly high (*9*).

An interesting example of unusual behavior during beating is the high resistance to fibrillation shown by kraft pulp oxidized with periodic acid (*10*), despite the fact that the viscosity of the pulp would normally indicate good beating characteristics. On the other hand, when the treated pulp is further oxidized with sodium chlorite, it regains its capacity to fibrillate during beating. Although viscosity measurements indicated a

rise from 6 to a little over 8 cp. when the pulp was treated with sodium chlorite, the average chain length —that is, the degree of polymerization—was probably substantially unchanged by the secondary oxidation (*11*). The increase in D.P. in this instance is only apparent since viscosity measurements in alkaline media are an unreliable index of the degree of polymerization of cellulose if the cellulose contains a high proportion of reducing carbonyl groups, as has been shown by Coppick (*12*).

Parmenter (*13*) points out that the viscosity test is of no value in predicting the relative papermaking properties of two different types of pulp and he suggests that, in addition to fiber length and other physical properties, pulp strength characteristics are dependent upon the hemicellulose content as well as on the average chain length of the cellulose molecule. On the other hand, he believes that a fairly direct relationship might be found between the viscosity values of several shipments of a given grade of pulp obtained from the same pulp manufacturer and the relative strength characteristics of these shipments.

Such observations emphasize the multiplicity of variables involved in papermaking. However, since for any given type of pulp, changes in degree of polymerization are ordinarily associated with changes in beating behavior typical for that pulp, viscosity measurements are important signposts in cooking and bleaching processes.

CHAIN-LENGTH DISTRIBUTION IN RELATION TO PAPERMAKING

In the discussion thus far, we have considered the viscosity and average D.P. of a representative pulp sample. The actual distribution of the individual molecules by degree of polymerization is at this time beyond the scope of our scientific attainment. The concept is approached as we convert a given pulp sample into a number of samples by fractional solution or fractional precipitation—for example, into fractions of decreasing average D.P. The greater the number of significant fractions, the more nearly the ideal is reached.

Considerable work has been done on the influence of chain-length distribution upon the physical and chemical properties of rayon. In line with the work done on rayon, it would seem that various pulps from different wood sources by the same or different pulping processes might show wide variations in their chain length distribution and that these variations might somehow be related to variations in pulp properties.

Attempts have been made to fractionate directly solutions of cellulose. One of these was reported by Straus and Levy (*14*), who described a method for the direct fractionation of a cupriethylenediamine solution of a pulp.

The first serious attempt to relate the chain-length distribution to pulp properties and processes was made by Atchison (*15*) who studied the influence of cooking and bleaching on the chain-length distribution of the total carbohydrate fraction in sprucewood. The distribution in wood was determined on isolated holocellulose which suffers little degradation during its isolation. The holocellulose was isolated by a modification of the method of Van Beckum and Ritter. The pulps were prepared from the wood by the sulphite, soda, and sulphate processes. The holocelluloses and pulps were converted to nitrates and the average chain lengths of the nitrates calculated from specific viscosity data, using the Staudinger conversion equation. The nitrates were fractionated by fractional solution using ethyl acetate and absolute ethyl alcohol in various proportions, and the viscosities of the fractions were determined.

The results show the carbohydrate fraction in wood to be heterogeneous, consisting mainly of low and high D.P. material. Pulping causes a disappearance of short-chain material and a degradation of long-chain material. The amount of medium chain-length material is thus increased. Such equalization occurs more in the sulphate than in the soda or sulphite process. Atchison believes that this fact, together with the higher noncellulosic carbohydrate content in the sulphate pulp accounts for its better strength.

Bleaching increases the heterogeneity of the cellulose. Of particular interest is the chain-length diagram of the holocellulose. This shows 75% of the carbohydrate to have an average D.P. of 2000—the top range of the test—whereas 18% has an average D.P. below 500. There is almost no medium chain-length material present. This high-molecular weight fraction is about the same as the relative quantity of alpha-cellulose and hemicellulose B, the less soluble hemicellulose fraction.*

Heuser, Shockley, and Kjellgren (*16*) applied the same technique to a study of the chain-length distribution of kraft pulps made from western hemlock, Douglas-fir, western red cedar, northern spruce, and loblolly pine. Step curves have been drawn to show the relationship between the degree of polymerization and the weight per cent of the fractions. Differential weight distribution curves were also included in the paper. All five pulps show about the same amount of low molecular weight material, ranging from 10% for pine and red cedar up as high as 16% for spruce and western hemlock. A somewhat greater difference is noted if we consider the material in the range of 1900 D.P. or higher. Here we have for red cedar and pine better than 55% of the material in this classification; the value for spruce is 50%, whereas western hemlock and Douglas-fir show approximately 35%. The authors, however, draw the conclusion that, "The method of fractional solution has its limitation and that for a more thorough separation of the high molecular weight fractions, other techniques will have to be used. It is apparent from the study that the distribution of molecular weight of cellulose, as measured by the method used, does not play any primary part in the physical properties of these pulps. The one pulp having an outstandingly different curve is that of western red cedar where 60% of the particular pulp is found in a very narrow range of polymerization degree between 1742 and 1996.

"The particular value of the pulp fractionation appears to be in the selection of pulps for rayon manufacture, for random distribution of molecular sizes is undesirable. The determination of the unfractionated viscosity is valuable in the control of a process using the same material for the preparation of a specific type of bleached pulp."

The opposite method of fractionation, based upon the

* From analytical data in the files of The Institute of Paper Chemistry.

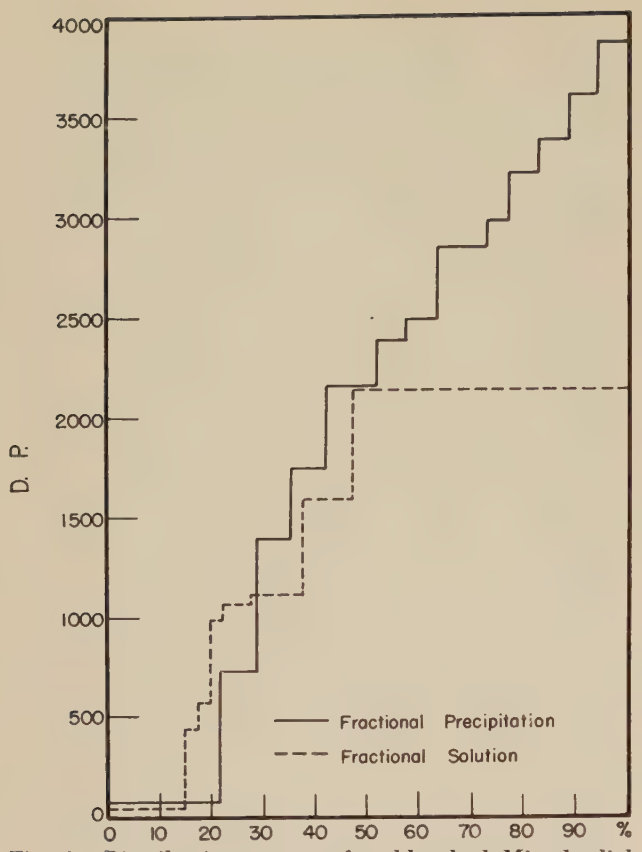

Fig. 1. Distribution curves of unbleached Mitscherlich pulp

fractional precipitation with water from an acetone solution of the pulp nitrate, is described by Tasman and Corey (*17*). The precipitate in this case was centrifuged and viscosity determinations were made on the supernatant liquid. Since the solvent viscosity is known for acetone-water mixtures, the relative viscosities can be calculated and the D.P. values can be determined from the intrinsic pulp viscosity values. Summative distribution data are presented for two pulps ranging from the average D.P. for the whole pulp of 1160 to 1180 down to 237 in one case for the average D.P. of the smallest fraction. The top D.P. is in the range of 2700. No attempt is made by the authors to relate their findings to specific pulp properties.

During the current year, Jörgensen published in book form an account of investigations carried out at The Institute of Paper Chemistry and at McGill University under the title of "Studies on the Partial Hydrolysis of Cellulose." The first part of this report deals with the fractionation of cellulose. The author has very carefully compared the fractional solution and the fractional precipitation method using cotton linters, and unbleached Mitscherlich spruce pulp and unbleached kraft pulp, a laboratory cooked, bleached and refined sulphite pulp, two commercial dissolving pulps—one for acetylation and one for viscose rayon—and, finally, a laboratory cooked bleached and refined pulp of low average D.P.

The difference in results between the fractional solution method and the fractional precipitation method is illustrated by Fig. 1. The fractional solution step curves show in the upper part one or two relatively large portions. In the fractional precipitation method this is not the case, but the fractions increase in D.P. for a considerable distance beyond the top values in the fractional solution method. The medium and low D.P. material seem also to be better separated in the fractional precipitation method.

In order to further test the two methods, Jörgensen subjected both the bottom and top fractions from solution fractionation (processes termed by him nonuniform and uniform) to further fractionation by the precipitation method. The results (Table I) showed that both fractions were heterogeneous in composition with a range of D.P. between 105 and 3110 for the nonuniform and between 460 and 3670 for the uniform portions. This demonstrated rather clearly the inadequacy of the solution technique.

As further proof of the value of the precipitation method, certain of the fractions separated by precipitation were blended and refractionated with surprising similarity in results. The final proof of both reproducibility and suitability of the precipitation method was demonstrated when the experimentally determined step curve for the Mitscherlich pulp was compared with a curve calculated from the chain length distribution of the refractionated upper and lower portions (Fig. 2). This method seems to be a tool of demonstrative value for developing information on the chain length distribution of the carbohydrate fraction in pulp.

The difference in results obtained with the two methods is explained by Jörgensen as follows:

"It is obvious from the above data that considerable difficulties are involved in the fractional solution technique—i.e., in extracting the shorter chain molecules from the cellulosic material. We must be aware of the fact that by using this procedure we are dealing with the cellulosic material in fibrous form and therefore

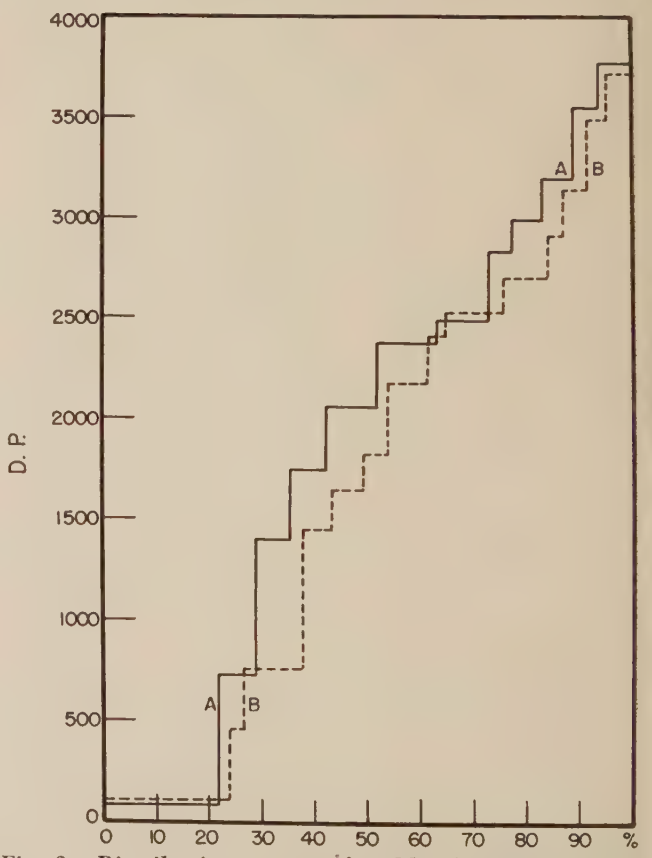

Fig. 2. Distribution curves of unbleached Mitscherlich pulp—a. Directly determined; b. Reconstructed refractionated fractions obtained by fractional solution and fractional precipitation techniques

Table I. Refractionation of the Mitscherlich Pulp Fractions Obtained by Fractional Solution Method

Fraction	*Weight, %*	*D.P. of fraction*
I. Refractionation of Mixture a (nonuniform portion) According to the Fractional Precipitation Technique		
1	43.2	105
2	10.2	760
3	8.6	1430
4	8.0	1825
5	6.8	2190
6	8.8	2520
7	5.6	2670
8	4.2	2895
9	4.6	3110
II. Refractionation of Mixture b (uniform portion) According to the Fractional Precipitation Technique		
1	6.6	460
2	12.8	735
3	14.8	1635
4	9.0	2130
5	7.0	2390
6	5.8	2480
7	12.4	2690
8	5.8	3100
9	8.6	3270
10	8.8	3460
11	8.4	3670

also with both its crystalline and its amorphous portions, at least in the earlier part of the fractionation procedure. It is to be expected that this fact will play an important role in the fractional solution of the material. Chains which entirely or partly belong to the less ordered areas must be expected to go into solution before chains in the higher ordered areas. The fractionation will therefore take place not only according to the chain length but also according to the position of the chains in the fiber. As the dissolving mixture becomes richer in solvent, the solid phase will lose its crystalline-amorphous structure and become a highly swollen mass. It is evident from the fractionation data that this swelling does not facilitate the fractionation. We may expect equilibrium conditions to exist on the surface of the swollen mass; chains on the surface, soluble in the solvent-nonsolvent mixture to which they are exposed will therefore go into solution. A network of longer chains, not soluble in this particular mixture, will remain in the surface layer and behave as a semipermeable membrane for the inner part of the swollen gel, and hinder smaller chains which are soluble to diffuse out into the solution. These chains will therefore not go into solution before the outer layer, consisting of the longer chains, are solubilized.

"The typical distribution curves obtained from the fractional solution techniques may be explained in accordance with the above theory. The first, or first two rather large low-molecular fractions consist of the shorter chains belonging to the less ordered areas. The next fractions are small and increase relatively rapidly in D.P. and consist of the short and medium chains in the outer layer of the swollen gel. The last large fractions have the same or even decreasing D.P.'s and consist of the longer chains in the outer layer of the gel, and the inner part of the gel which consists of all lengths originally present in the material, with the possible exception of the smallest chains, which were dissolved when the solid phase still had its fibrous state.

"The above theory is well supported by the results from the refractionation, using the precipitation technique, of fractions obtained in the fractional solution method, where it was found that the apparently uniform upper part of the distribution curve obtained by fractional solution consisted of chains of all molecular weight species present in the material except the lowest. Experimental evidence has shown that very little is gained in destroying the fiber structure of the material before fractionation, by for example casting a film of the material. The state of a highly swollen gel is only reached at an earlier stage in the fractionation procedure."

Jörgensen has not attempted to relate his distribution curves to the properties of the specific pulps used, other than to point out the significance of the absence of low molecular material in the two dissolving pulps; however, the sharp differences between cotton linters and ordinary wood pulps are clear from a comparison of the curve for linters with those for the Mitscherlich pulp, the sulphite pulp, and the unbleached kraft pulp. Cotton linters show no material of a D.P. below about 350 and no material of D.P. above 2400. A significant amount of Mitscherlich pulp (22% to be exact) has an average D.P. of 105, and about the same amount has a D.P. above 3000. Likewise the sulphite pulp shows about 20% below 200 and at least 7% above 3000. In the case of the kraft pulp there is 23% with an average D.P. of 165 and 7.8% above 3000. The preparation of the pulp of termed "low average D.P." is clearly seen to consist in the removal of material of D.P. above 1500, ending up with significant percentage of the pulp with a D.P. between 250 and 1000—better than half being in this range. It would seem as though the way is open to extend our knowledge of the importance of molecular weight distribution on pulp properties through the use of the techniques described by Jörgensen.

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The Elastic and Rheological Properties of Papermaking Fibers

Some of the Problems to Be Met in Developing an Analytical Approach to the Subject

J. A. VAN DEN AKKER

Fiber-to-fiber bonds probably have rheological properties, however, the thickness of a zone of bonding is so slight that, as a first approximation, it seems reasonable to assume that strain occurring at a bond is essentially that of the associated fibers. Thus far, the work on rheological and elastic properties of paper has been done with the view that paper is to be regarded as an entity rather than the effect on the components and the paper structure. It is generally agreed that the strength of a typical paper resides primarily in the fiber-to-fiber bonds. The several theories of binding are discussed. Closely associated with the number of fiber-to-fiber bonds is the bonded area, the methods of measurement of which are under question. Ultimately, it is desirable to compute the appropriately averaged stress and strain in the fibers and the average shear stress in the fiber-to-fiber bonds. Flexural rigidity of the fibers and the effect on the sheet are considered. The various factors are discussed and suggestions as to an approach to the general problem are made.

RESEARCHES in the mill underlying the mechanical properties of paper will depend in large measure, in my opinion, on the fulfillment of certain needs: First, it will be desirable to develop a special statistics to handle the complex problems presented by the structure of paper. Second, information is needed on the elastic and rheological properties of papermaking fibers. With regard to this need, we take it for granted that mechanical studies of individual fibers are apt to be statistically incorrect and that the cost of studying the very large number of fibers required in a reasonably accurate evaluation of a single sample would be inordinately great; hence, it is hoped, the development of a special statistical mechanics will enable one to infer certain properties of the fibers from measurements made upon the paper sheet. Third, more accurate information is needed on the intrinsic strength of the fiber-to-fiber bonds in paper. It may be remarked, incidentally, that the fiber-to-fiber bonds probably have rheological properties. However, the thickness of a zone of bonding is so slight that, as a first approximation, it seems reasonable to assume that strain occurring at a bond is essentially that of the associated fibers.

These and similar thoughts must have been mulled over in the minds of many of the technical men of the industry. The problem is obviously an intangible one, and it is regretted that the present discussion can do no more than to focus attention on certain aspects of the analytical approach.

The excellent work of recent years on the load-elongation characteristic of paper and its relationships with the utilization of paper, carried out by Gibbon (*1*), Farebrother (*2*) and, most intensively, by Steenberg and his collaborators (*3–10*), Mason (*11*), and Rance (*12*) has, without doubt, given us valuable new tools of measurement and techniques for interpretation which will enable the industry to understand better the relationships between use requirements and the properties of paper on the one hand and between paper machine and other processing variables and the properties of paper on the other hand. Leaderman (*13*) gives a technical but very readable account of the development of experimental techniques and theory for studies of the elastic and viscous properties of materials generally. Excellent discussions of the application of the concepts and techniques of this field to the evaluation of paper have been given by Steenberg and his associates (*3–6, 10*), who also have developed the application to paper of the Eyring-Halsey theory.

Thus far, the work on rheological and elastic properties of paper has been done with the view that paper is to be regarded as an entity; that is, the various investigators have treated paper as a sheet of material without regard for analysis of the influence of its components and the effects of its structure on the observed macroscopic properties. This view is satisfactory where one is concerned primarily with the evaluation of the finished product in the light of use requirements and, of course, one may study the influence of various processing variables on the macroscopic properties. However, our contacts with the problems of the industry have intensified our conviction—shared by many in the industry—that we should strive toward an analysis which would help us to separate the fundamental variables of sheet structure and fiber properties. This is, of course, an essential aspect of a scientific approach to any problem.

It has already been observed that the mechanical analysis of paper is an intangible one. Numerous studies with the microscope have shown that the fibers of paper are felted together with all but the shortest fibers lying in surfaces that are nearly parallel to the sheet. None of the fibers is straight; all are curved, bent, or kinked in a large variety of shapes. The distribution functions for length and cross-sectional area of the fibers are broad, but are presumably characteristic for the paper under study. It is well known that the fibers are not randomly oriented in machine-made paper, but that the distribution function for direction (relative to the machine direction) displays a maximum in the machine direction and a minimum in the cross-machine direction; the function is more isotropic on the felt side than on the wire side, where the preferential align-

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ment appears to be most strong. Recently, Danielsen and Steenberg (*14*) have published data on fiber orientation which enhance the quantitative aspects of these facts. The individual fibers are not simple bodies; coarse and fine fibrils have been torn from the fibers by the beaters, jordans, etc., and observation with the electron microscope has revealed that there is almost no lower limit to the fineness of the fibrils. These fibrils and fragments of fibers add much to the paper and to the complexity of the problem. Paper usually contains nonfibrous components such as clay, starch, rosin size, etc. Each fiber lies in contact with, or in near contact with, many other fibers. At numerous points of contact, it is generally believed that relatively strong bonds exist. In view of the very small effective pore size of most papers (of the order of 10^{-4} to 10^{-5} cm.), the average fiber is undoubtedly bonded to a fairly large number of other fibers. Thus, for each fiber that is stressed during a mechanical test, many fiber-to-fiber bonds are stressed. This hastily sketched picture of a paper sheet is essentially that which most technical men in the industry visualize as fitting qualitative observations. It is not a simple picture; by comparison, the complicated analysis of forces and moments in a steel bridge is relatively straightforward. The problem presented by paper is seen at the outset to be too complicated to be amenable to traditional structural analysis. As stated in the introductory remarks, there is need for the development of a special statistics. The kind of special statistics needed will be clearer to those who have studied the kinetic theory of gases and statistical mechanics. No reference is here made to conventional statistics.

It now appears to be generally agreed that the strength of a typical paper resides primarily in the fiber-to-fiber bonds. Numerous as these bonds are, failure evidently initiates in them rather than in the fibers. It has long been recognized that the breaking length of paper (typically of the order of magnitude of 5000 meters) is far less than that of wood pulp fibers. Klauditz, Marschall, and Ginzel (*15*) have recently shown that the breaking length of wood pulp fibers is of the order of magnitude of 40,000 meters. Of course, the near-random orientation of fibers would account for a lessening of the maximum possible breaking length of paper, corresponding to infinite bonding strength. At one time, there were a number of proponents of the theory that the strength of paper resides in the interweaving of fibers and fibrils, as in a twisted textile thread. There are several observations that argue against this theory. One is that paper made from a well-beaten pulp is extraordinarily weak when the water in the wet web on the forming wire is replaced with a nonpolar liquid (e.g., when treatment is made with acetone followed by butanol). Another is the fact that certain special pulps, which fibrillate extensively on beating, will not yield strong paper when both the beating and the sheet forming are done in the presence of water. Perhaps the strongest argument of all against the mechanical binding theory is found in the recent work with load-elongation curves. Paper exhibits both "primary creep" and "secondary creep," the latter being an irreversible extension occurring on the first straining of the paper. Steenberg has shown that a strain-hardened paper (from which secondary creep has been removed) will withstand repeated straining and relaxing without damage to its structure. This behavior would not be expected if the binding in the paper were primarily of a frictional nature. Furthermore, the load-elongation curves obtained by Steenberg and his associates were shown by them to be in accord with the theory of Eyring and Halsey, which does not embrace macroscopic slipping. In this discussion we should recall the well-known theory of Campbell, which accounts so convincingly for the drawing together of fibers during drying, thus explaining the close approach of surfaces—within molecular dimensions—needed for hydrogen bonding.

Considerations on the nature of failure of paper under tension prompted an experiment on the sounds generated in a paper strip during straining to the rupture point. Preliminary work has been done with the arrangement shown in Fig. 1. A paper strip (*S*) is

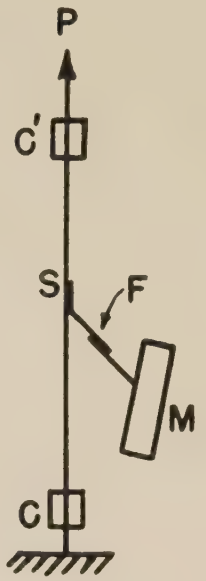

Fig. 1

mounted in clamps (*C*, *C'*), the lower one of which is fixed. To avoid the confusing sounds of auxiliary mechanisms, the movable clamp (*C'*) is pulled by hand. A suitable linkage between the center of the strip and the diaphragm of a microphone (*M*) may be easily and effectively obtained by means of a narrow strip of paper cemented to the paper strip by means of a rubber cement, and a narrow strip of thin brass shim stock cemented with cellulose cement to the diaphragm. The linkage must be capable of extension because of the appreciable movement of the center of the paper strip during straining. To this end, the strip of paper and the strip of brass shim stock are adhered together at *F* with a thin film of "Vistanex," or other viscous liquid having a viscosity of the order of 2000 poises. Such a joint readily transmits audio-frequency sounds and sharp pulses. It is important that the linkage between the diaphragm and the test strip (*S*) be away from the clamps, because sounds generated in the paper during straining would be deadened by the inertia of the clamps. The microphone is connected to a high-gain amplifier, the output of which is connected to head

phones. On "listening" to several strips of rag bond and sulphite tablet paper during straining, no sounds were heard up to almost the rupture point, at which, of course, a loud "pop" was heard. In a few instances, the failure might have been preceded by a very few discrete "pips," but if such existed, the time interval between their occurrence and the break was very short. There was no general hissing, rushing, or crackling sound of the sort one might expect if the paper were held together primarily by mechanical, frictional forces. No doubt, there are certain tissue papers and papers prepared from essentially unbeaten stock which will emit sounds during an appreciable portion of the straining. Experiments on materials other than paper should also be interesting.

We have already had occasion to point out that the average fiber in paper is bonded to a fairly large number of other fibers, so that the intrinsic bonding strength is not required to be exceptionally high in paper of ordinary strength. A precautionary note should be injected here. It might be argued that fibers would fail before the rupturing of bonds in a hypothetical paper containing very long fibers, on the ground that each fiber would be so well attached to other fibers. Failure, of course, initiates in a zone where the local stress and strain are high. In such a zone, the fibers become elongated beyond the average value, and bonds in and near the zone become involved in a stress concentration that could cause them to fail, irrespective of what length of fibers and what number of bonds extended beyond the zone. This point is well illustrated by the data of de Bruyne (*16*), whose experiments showed that the strength of a glued joint is not proportional to the length of the glue line parallel to the axis of the stress; beyond a certain point, there is little gain in strength with increasing length of the glue line. Extensibility of the members which are glued together causes a stress concentration in the layer of glue. Perhaps these considerations account for the fact that the tensile strength of paper is only a low function of fiber length.

Closely associated with the number of fiber-to-fiber bonds in paper is the bonded area. Evidently a factor which should be useful in at least our current attempts to gain a better understanding of the properties of paper is the fraction of the external specific surface of the fibers that is involved in bonding. Parsons (*17*) has developed and Ratliff (*18*) has utilized an optical method which, at the present time, appears to offer the only means for estimating this fraction. This method is based on the notions that (a) where two fibers are in optical contact, there is also a bond and (b) the specific scattering coefficients of bonded and unbonded (butanol-formed) papers, calculated by means of the Kubelka-Munk theory, are proportional to the total external surface areas of the fibers which are not in optical contact. Both assumptions are vulnerable, and it is not believed that the technique offers an accurate measurement of the bonded fraction. However, we believe that the method has been of value in certain of our investigations.

Engineering concepts developed in the field of strength of materials should not, in my opinion, be applied to paper or to paperboard without exercising certain precautions. As we have already recalled, paper is heterogeneous in a number of important ways. Particular reference will not be made to the porous nature of paper. The calculation of stress from load and the cross-sectional area of the test strip affords a good example of the pitfalls that lie in the path of one who proceeds in a straightforward manner with the principles that apply so usefully to homogeneous materials. Overlooking, for the moment, the difficulty in defining and measuring the thickness of paper, we become confronted with the significance of "apparent stress." The thickness of paper may be modified (as by compression in the dry state) without substantial change in the load-elongation characteristic; however, if we were to compute the stress-strain curves, we would find that such modification had changed the stress-strain relationship. Our conclusions would then be erroneously affected.

Ultimately, we wish to compute the appropriately averaged stress and strain in the fibers and the appropriately averaged shear stress in the fiber-to-fiber bonds. In a first attempt, one naturally seeks to calculate the cross-sectional area of the fibers. The following considerations illustrate a very elementary aspect of the sort of statistical treatment to which reference was made earlier. Let there be N fibers per unit area of the sheet, having definite distribution functions with respect to length, cross-sectional area (of cell wall), and orientation. We shall use a model in which the fibers are straight. The probability that a fiber will be oriented at angle θ, in the range $d\theta$, will be $P_\theta d\theta$; that its length will be x, in the range dx, will be $P_x dx$; and that its cross-sectional area will be a, in the range da, will be $P_a\, da$. The total number of fibers in the sheet in this class will be $N\, b\, c\, P_\theta\, P_x\, P_a\, d\theta\, dx\, da$, where b is the vertical dimension of the sheet (the sheet is visualized as held vertically), and c is the horizontal dimension. We now imagine cutting across the sheet horizontally at any level, designated by a line AA'. The probability that any fiber in the foregoing class will be cut is $(x \sin \theta)/b$. The area produced in each fiber in the class that is cut is $a/\sin \theta$. Hence the total area produced in the foregoing class by the cut is $N\, c\, a\, x\, P_\theta\, P_x\, P_a\, d\theta\, dx\, da$. When this expression is integrated to encompass all the values of angle, fiber length, and fiber cross-sectional area, and the result is divided by c, we obtain, for the total cross-sectional area produced by the cut per unit width, $N \int a\, x\, P_\theta\, P_x\, P_a\, d\theta\, dx\, da$. When this is done for a cut BB' parallel to the vertical direction (maintaining θ relative to the same axis as before), the same expression is obtained. Also, it would appear that a given load applied in each of the two principal directions of the paper would produce the same stress in the machine direction and the cross-machine direction.

The foregoing use of the cross-sectional area of the fibers to compute the stress in the fibers is probably not accurate. The fibers form a complicated network, in which the small meshes are of irregular shape. If two segments of fibers, each making a large angle with the direction of the applied load, alone carry the local load, then the force in each fiber would be larger than that corresponding to parallelism with the load by the factor $1/\sin \theta$. However, this situation is not regarded as typical; it seems more likely that nearby segments that make small angles with the direction of the applied load would bear the brunt of the local load and that segments making large angles with the applied load

would actually experience a greatly reduced tension. The difficulty that is apparent here is essentially the major difficulty that should be overcome in the development of an analytical approach.

One consideration of the small meshes of the network appears fairly clear. Persons discussing this subject seem almost inevitably to resort to greatly simplified models such as that of a network comprised of two intersecting sets of parallel lines making an acute angle in the machine direction and an obtuse angle in the cross-machine direction. Here the major axis of each mesh is in the machine direction. Evidently the major axis of the meshes in paper is in the machine direction because of the preferential orientation in that direction. As a consequence of the geometry of the configuration, a given load should result in a greater observed strain in the cross-machine direction. This is not to say that the greater strength in the machine direction is altogether the result of the preferential orientation. In a very interesting series of papers, Edge (*19–21*) presents the results of his observations on the importance of wet stretch and of tension during drying to the tensile strength of the paper. As an illustration of the magnitude of the effect, Edge prepared handsheets (random fiber orientation), subjected them to a carefully controlled wet stretch and then caused them to dry under tension. The ratio of tensile strengths in the two principal directions attained a value as high as 4:1! In another series of experiments, specimens of the web were taken from a paper machine which had been stopped for the purpose. A specimen from the wire had nearly equal strength in the two directions; specimens taken from the wet felt displayed an appreciable asymmetry; and the ratio of machine direction to cross-machine direction strengths for specimens taken at the first drying cylinder was large. Steenberg, in a discussion with Edge, suggested that the wet stretch and tension might well have caused the fine fibrils at the surfaces of the fibers to have become aligned, thus resulting in a stronger bond in the machine direction (*21*). The findings of Edge should be taken into account in an analytical approach to the problem; it appears that the fiber-to-fiber bonds do not have the same strength for all directions of shear.

Another effect which should be allowed for is that designated by Steenberg as "micro-creeping." He illustrates this effect, to which he attributes secondary creep, in a figure showing the segments of fibers as curved and wavy in paper which has not been strained, and straight in paper that has been strain hardened (*7*). Because of the wavy nature of the fibers, the extensibility displayed by the paper on the first stressing is greater than that observed in later cycling of the strain.

It seems to me that an important part of the increase in tensile strength—increase in the whole load-elongation curve—caused by drying under tension is the equalization of distribution of stress among the fibers. When the moisture content is high, the fibers and fiber-to-fiber bonds are in a relatively plastic state; hence, during the drying process, tension causes fibrous elements between points of bond to become straighter and, because the sheet is in a plastic state, all fibrous elements partake more equally of the load than would be the case in the absence of tension. When the paper dries, this condition becomes frozen-in. The frozen-in stress does not refer to a residual net tension or compression in the sheet but, rather, to a freezing-in of differential effects within fibers. For example, a fiber which had been constrained during drying in a shape that is different from that which it would have assumed in a free state possesses frozen-in tension and compression stresses. When the paper is subjected to strain, stress will arise in this fiber more readily than would have been the case in the absence of the constraint during drying. If the paper is dampened, the fiber will tend to change its shape, although the restraining effect of neighboring fibers to which it is bonded may prevent the fiber from reverting to its original condition. Incidentally, it seems reasonable to suppose that some of the phenomena of hygroexpansivity of tension-dried paper may be partially explained by frozen-in stresses and the tendency of fibers to revert to their natural configurations when the moisture content of the sheet is increased.

This relative tightness and looseness of the fibrous elements in a sheet of paper (which should be most pronounced in paper which has not been dried under tension) is a complicating factor which should not be overlooked in any analysis of the stresses and strains occurring in the fibers. [Generally speaking, stress concentration is too often overlooked. Even in the ordinary testing of paper and other materials, stress concentration on a gross scale is not the sort of thing that meets the eye. Good accuracy of measurement may be sought, but a systematic imperfection—such as faulty clamps, poor sheet formation (over which the laboratory technician has no control), presence in the paper of shives and other imperfections—may result in local stress concentration which causes premature failure at a load very much less than would be observed under more ideal circumstances; yet, the situation is usually not recognized, and the hidden error may be very much larger than that corresponding to the statement of accuracy of the work.]

Softness of paper is a difficult thing to define; in fact, it evidently has several definitions within the paper industry, depending upon whether one is discussing facial tissue, book paper, bread wrap, etc. Certainly, in all cases, rheology is important. But a load-elongation curve alone cannot yield an instrumentally determined quantity which could be expected to correlate accurately with subjective judgment, because other factors are involved. Important among these are flexural properties (which, fundamentally, call into play the same rheological properties as those observed in pure tension), the thickness of the paper, and the diameter of the fibers. Earlier, we had occasion to warn against the use of sheet thickness in computing "apparent stress." However, until a satisfactory analytical approach to the problem has been worked out, we must employ both the sheet thickness and the apparent modulus of elasticity because, for geometrical reasons, thickness has a profound effect upon the flexural-rigidity of a sheet material. In improving upon the elementary approach to the problem of stiffness of paper, one might well allow for the probability that the effective modulus of elasticity varies from the wire side to the top side of the paper. However, no information on this variability of the modulus of elasticity through a sheet of paper seems to be available.

The technical men representing quite different segments of the industry often have occasion to speak of the influence on flexural rigidity of the use of southern or certain western fibers which are coarser and more "brash" than are the wood fibers from the north. Anyone who is inclined to treat paper as a homogeneous sheet material may be dismayed to learn that coarseness of the fibers is important to flexural rigidity of the sheet if, as is probably the case, the elastic and rheological properties of the cellulose comprising the southern and northern wood fibers are similar. We have here another example of the difficulties that are encountered in regarding paper as a homogeneous sheet material. Let us discuss, in a qualitative way, certain of the aspects of paper stiffness, as the thickness of the sheet is increased from quite small to very large values. We may start with essentially a mono-fiber sheet—i.e., a sheet which is one fiber thick except in regions of bonding. It is clear that the flexural rigidity of such a sheet will depend importantly on the stiffness (flexural rigidity) of the fibers *per se*. Now, if we imagine that the sheet thickness is built up, and that the fibers in the various layers are well bonded together, we approach the condition usually treated in the field of strength of materials: The fibers farther away from the neutral surface contribute more importantly to the flexural rigidity of the sheet, and the contribution of these fibers is now more important through tension and compression of fiber elements (as opposed to simple bending). If it were not for the resistance of a sheet to shear (with the shear force parallel to the sheet), the flexural rigidity of the sheet would be simply the summation of that of the fibers, and the sheet stiffness would be proportional to the first power of sheet thickness. However, in paper that is well bonded, the stiffness tends to approach variation with thickness raised to the third power, as the thickness is increased. Perhaps our main conclusions from this discussion of stiffness are the following: (a) care must be exercised in applying engineering formulas in studies of the stiffness of paper, (b) the stiffness of thin papers depends primarily on the flexural rigidity, *per se*, of the fibers, as well as on their rheological properties in flexure, and (c) the stiffness of thick papers depends primarily upon the elastic and rheological properties of the fibers in pure tension and compression. It seems likely, then, that the "brashness" of the fibers would have a more profound effect on the softness of paper in the case of quite thin papers. Possibly, in the case of heavy papers, the flexural rigidity and softness of the sheet are less a matter of individual fiber stiffness, and more a question of extensiveness of fiber-to-fiber bonding. There is a great deal of evidence favoring this latter statement.

Folding, creasing, and folding endurance are properties of paper of very great importance. Yet they are difficult to define and to measure. Similarly, they are difficult to approach in an analytical manner. The testing almost always involves disruptive strains. It seems highly probable that fiber-to-fiber bonds are gradually broken in the endurance tests, but the question of how much of the failure of the sheet is attributable directly to failure of the fibers under repeated straining is an important one. If fibers become embrittled because of natural or accelerated aging, or because of chemical degradation, the folding endurance of paper comprised of the fibers declines markedly. Can enough strain occur in a fiber-to-fiber bond to cause the bond to fail prematurely because of such degradating actions? In my opinion, it seems likely that the failure initiates in the fibers where the degradation has been severe.

In concluding, the author should like to express the hope that real attempts will be made to develop some sort of special statistics of the mechanical properties of paper which will be of value in yielding accurate data on the elastic and rheological properties of papermaking fibers, and on the intrinsic strength of the fiber-to-fiber bonds in paper.

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The Specific Surface of Fibers—Its Measurement and Application

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The specific external surface area of pulp fibers is a fundamental property of considerable importance. Of the various methods of measurement applicable to particulate systems in general, only the microscopic, the Clark silvering, the optical, and the fluid-permeability methods have been used with any success on pulp fibers. The last three methods are reviewed and, to illustrate the application of each, representative results obtained by various workers are presented, particular emphasis being placed on the permeability method.

Paper consists of an aggregate of initially separate fibers and fiber fragments united by an interpenetration of the surface molecules in such a way that a continuous plastic network is formed. It is therefore natural that an understanding of the relationship between the properties of the constituent fibers and the composite properties of paper requires some knowledge of the surface characteristics. Obviously, one such characteristic is the surface area since this represents in a sense the potential capacity of the fibrous mass to form bonds. The specific surface is important for a number of reasons in addition to its supposed relation to paper strength. In the wet state the surface area is directly related to the drainage characteristics of the pulp, and its capacity to retain fillers, dyes, pigments, sizing materials, resins, and other additives. The unbonded, or free, fiber surfaces in paper determine a number of properties among which may be cited reflectance and opacity, porosity, absorption, retention of printing inks, and other printing properties.

The measurement of specific surface of particulates is of interest in many scientific and technological applications and has received considerable attention. Numerous methods have been proposed and used. They include the sedimentation rate, gas and solute adsorption, radioisotope exchange, microscopic, surface catalytic, optical, and permeability methods. Measurements made by gas (*1*) and solute adsorption (*2*) are reported in isolated instances, but only the last four methods listed above have been used to any extent on pulp fibers. The microscopic method (*3*), in which areas are computed from measured fiber dimensions, is not only tedious but is limited in application to fibers of well-defined and simple shape. The remaining three methods are discussed below and some typical results presented. Since the permeability method is relatively new and shows considerable promise, it is discussed in somewhat greater detail.

SURFACE CATALYTIC METHOD

This method, devised by Clark (*4*), modified by McEwen (*5*), and adopted as a suggested TAPPI Standard Method (T 226 sm-46) is the most widely used and probably the most familiar in the pulp and paper field. Briefly stated, it consists in depositing on the surface of the fibers a continuous film of colloidal silver to a depth of up to 2 mu, and measuring its catalytic activity in decomposing hydrogen peroxide under standard conditions. The silver is precipitated from ammoniacal silver nitrate by the reducing action of the fiber. The decomposition of the peroxide is a first-order reaction whose velocity constant is assumed to be proportional to the surface area of the catalytic film which is identified with the fiber area. The proportionality constant was established by Clark (*4*) by calibrating with similar films deposited on directly measured areas of cellophane, and correction factors for the effect of temperature provided.

In using the method, it is essential that scrupulous cleanliness be observed to avoid the inclusion of the numerous promoters and inhibitors of this reaction. It has been shown (*4, 5*) that the catalytic activity is not critically dependent upon the thickness of the film provided a minimum value is exceeded.

The assumption that the specific activity of the silver film is constant and independent of the size and curvature of the particle, is probably not strictly valid, especially with small particles such as fines. This objection, however, is a minor one. The real difficulties are experimental and the most serious is the tendency, particularly marked with fines and fibrils, to agglomerate and yield spuriously low specific surface values. This difficulty has been reported (*6*) with moderately and highly beaten stocks. In such cases the results were very erratic and in some instances indicated a spurious decrease in specific surface on beating. Browning and Baker (*7*) have recently described several minor improvements in procedure which lead to more consistent behavior with beaten pulps.

In spite of these objections, this method remains the most convenient and rapid technique of determining the specific surface of water-swollen pulps. It is probable that additional improvements in the experimental procedure can be found which will add to its usefulness.

Values taken from Clark's paper (*4*) are given in Table I to indicate the order of magnitude of values obtained for several pulps.

By the method of mixtures, Reed (*8*) has shown that the measured specific surface of a whole pulp equals the sum of the measured values on the fractionated components. This is a partial substantiation of the validity of the method.

Browning and Baker (*7*) found a rough correlation between the increase of bursting strength and specific surface resulting from beating several species of unbleached kraft pulps. The specific surface-burst pres-

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sure curve was initially linear but subsequently appeared to level off at a constant value of the specific surface. The rate of development of specific surface decreased progressively with time of beating, an effect

Table I. Typical Results of Silvering Method Reported by Clark (*4*)

Pulp	*Specific surface sq. cm./g.*
Southern pine kraft, unbeaten	6,400
Swedish sulphite, unbleached, unbeaten	12,000
Fine groundwood	18,600
Beaten sulphite (commercial stock)	31,000
West coast sulphite, bleached, unbeaten	8,800
West coast sulphite, 4 r.p.g. kollergang	10,700
West coast sulphite, 8 r.p.g. kollergang	12,100
West coast sulphite, 32 r.p.g. kollergang	13,600
West coast sulphite, 64 r.p.g. kollergang	17,200

attributed to losses of up to 16% of the fines in the process of measuring the surface. Since the fines possess a large fraction of the total surface, the significance of the correlations is not clear.

OPTICAL METHODS

A beam of light traversing a pulp suspension is attenuated mainly by diffuse scattering at surfaces where there is a marked discontinuity in refractive index as at the fiber surface and, to a lesser extent, by absorption in the fibers and the liquid medium. The transmission coefficient of the suspension is thus a function of a number of variables, including the surface area. To a first approximation, which neglects absorption and secondary scattering effects, and providing the particles are not too small, we may write

$$\log T = -asc\sigma \qquad (1)$$

where

- T = fraction of light transmitted
- σ = surface area per gram of scattering material. This is identified with the external surface area of the fibers. Internally refracting regions are considered not to contribute to scattering, an assumption which weakens the principle of the method
- c = consistency (more properly the concentration) of the suspension
- s = a complex coefficient which depends upon the wave length of the light, the refractive indices at the scattering interfaces, and the shape, "color," orientation, surface roughness, and size of the fibers. For a given species of pulp s is assumed constant
- a = a "geometry" factor determined by the optical arrangement

This method was studied some years ago (*9*) but was found, with the rather crude experimental methods then available, to be of limited applicability. Measurements on aqueous pulp suspensions obtained in this way did, however, show consistent and reproducible increases in the external surface area caused by beating, the increase being roughly proportional to the time of beating.

A considerable improvement of the principle has since been made by Van den Akker and his associates working at The Institute of Paper Chemistry (*10, 11*). In these studies, the scattering coefficients of pads of dry fiber and sheets of paper were determined directly from reflectance measurements made with a Hardy spectrophotometer. Suitable corrections for absorption and secondary scattering made it possible to determine a specific scattering coefficient, S', corresponding to the product $s\sigma$ in equation (1) to a high degree of precision.

Ratliff (*11*) found that, for a given species of pulp, the scattering coefficient S' of unbonded pads of fibers, accommodated by solvent exchange from water to butanol and dried, was proportional to the specific surface (water-swollen) as determined by Clark's silvering method. The proportionality constant, which varied from one type of pulp to another, presumably because of minor variations in refractive index, internal optical properties, surface roughness, color, etc., of the fibers served as a calibration factor.

By comparing the S' values of unbonded fibers with those of bonded fibers in handsheets, and assuming that bonded portions are in optical contact and do not constitute scattering surfaces, Parsons (*10*) and Ratliff (*11*) were able to estimate the fraction of the external surface area of fibers entering into fiber-fiber bonding under various conditions of wet pressing, beating, hemicellulose content, etc.

Of the many interesting conclusions drawn from the data, perhaps the most significant is that the tensile and bursting strengths, modified either by wet pressing or beating, are roughly proportional to the amount of bonded area, until a saturation value is reached; subsequently no further increase in strength results. It was concluded (*11*) that, in this region, rupture is due to intra- rather than interfiber failure.

The results of a typical run in a Lampén ball mill taken from Ratliff's paper are shown in Table II.

Table II. Ratliff's Data on Development of Total and Bonded Area by Beating

Beating time, min.	*Exposed surface, sq. cm./g.* — *Unbonded sheet*	*Standard handsheets (scattering coefficient)*	*Percentage of area bonded*
0	9,200	4700	49
20	9,700	3200	67
40	10,600	3000	72
75	16,200	2900	82
95	19,000	2900	85

The fraction of the total area entering into bonding is surprisingly high, particularly for the unbeaten material. A probable source of inaccuracy, apart from the complex optical principles involved, is the manner of computing the total surface area of the unbonded fibers. In drying from butanol, which has a low swelling action, the fiber shrinkage is probably considerably less than in drying from water. Thus one might expect the butanol-dried areas, both internal and external, to be higher than if the fibers had been dried from water and kept separated. Despite this objection, these results are of considerable value and, with one exception mentioned later, represent the only information known to the author of the fraction of the available surface utilized in fiber-fiber bonding.

THE FLUID-PERMEABILITY METHOD

This method is now widely used for various materials and many papers have been published on its application. An excellent review of general principles and typical results obtained up to 1941 has been made by Sullivan

and Hertel (*12*). Since that time, a number of additional papers have been published, confirming the general applicability of the method and dealing with additional refinements in principles and techniques.

Principle of the Method

The basic principle of the method, of particular interest to papermakers since it relates to the mechanics of water removal in forming paper (*19*), is simple and is outlined below.

The rate of viscous flow of a fluid through a bed of porous material under the action of a hydrostatic pressure whose gradient is directed across the bed is given by Darcy's law

$$Q = KAp/\eta L \qquad (2)$$

where

Q = volume rate of flow through the bed
p = pressure drop across the bed
A = bed cross-sectional area
L = bed depth
η = viscosity of the fluid
K = permeability coefficient of the bed

The permeability coefficient K, which has the physical dimensions of area, is determined solely by the geometry of the network through which the fluid flows. If the number, size, and arrangement of the channels or pores and the laws governing flow through a single pore are known, K can, in principle, be calculated. Thus, for a highly idealized structure, consisting of a network of parallel cylindrical capillaries of identical radius r arranged along the axis of the bed, it is readily shown from Poiseuille's law that

$$K = \frac{1}{2S_o^2} \frac{\epsilon^3}{(1 - \epsilon)^2} \qquad (3)$$

Here ϵ is the fraction of the total volume (solid plus pores) occupied by the pores, and S_0 is the surface area of the walls of the capillaries per unit volume of the solid material through which the capillaries pass.

Thus if K and ϵ are known, S_0 can be calculated. Equation (3) is a particular form of the Kozeny-Carman equation (*12*) which serves as the basis of the permeability method.

Proceeding to the more complicated cases of distributed pore sizes, oriented at various angles to the axis of the bed, interconnected with one another, and having such diverse cross sections as ellipses, rectangles, slits with parallel sides, triangles, etc., equations can be derived having the generalized form of the Kozeny-Carman equation:

$$K = \frac{\overline{\cos^2\theta}}{k_0 S_0^2} \frac{\epsilon^3}{(1 - \epsilon)^2} = \frac{1}{kS_0^2} \frac{\epsilon^3}{(1 - \epsilon)^2} \qquad (4)$$

where k_0 is a shape factor characteristic of the channels, θ is the angle between the direction of a channel and the axis of the bed, and $\overline{\cos^2\theta}$ is averaged over all configurations. In a bed composed of particles of a particular shape, the shape factor and the orientation factor $\overline{\cos^2\theta}$ are considered to be constant and are combined as a single factor $k = k_0/\overline{\cos^2\theta}$.

The calculation of S_0 therefore depends upon using a value of k appropriate to the bed.

In beds of nonconsolidated particles, such as powders and fibrous materials, the pore structure is more complex than in any of the model networks mentioned above. Nevertheless it can be demonstrated by generalized hydrodynamic reasoning (*12*) that equation (4) should be valid, provided that the void fraction is below a critical minimum value which has been found experimentally to be about 0.85 for a number of different bed materials. At void fractions in excess of this minimum, the shape factor k increases with increasing void fraction.

Carman has shown that, for beds composed of randomly packed powders, the shape factor $k = 5.0$ and that equation (4) can be used to calculate specific surfaces within 3% of their values obtained by direct measurement. Fowler and Hertel (*15*) found excellent agreement between the areas calculated from microscopic measurements and permeability measurements on randomly packed plugs of cotton, wool, rayon, and glass wool fibers using a value of $k = 5.55$.

In applying equation (4) to beds of unconsolidated particles the following points should be borne in mind:

1. The surface area calculated is that presented by the bed material to the flowing fluid. In the case of discrete fibers, flow presumably occurs around, and not through, the fibers; and the area thus measured is the external surface. Strictly speaking, it is the area of the envelope of zero fluid velocity, and might more logically be called the "hydrodynamic surface."
2. The contact area between the particles is assumed to be a negligible fraction of the whole.
3. The void fraction ϵ used in the equation is that available to the moving fluid. There must therefore be no "closed" pores in the bed. Since the surfaces in such pores do not contribute to the resistance of the bed, an ϵ value determined from density considerations in such cases would be spuriously high.

In the case of nonswelling solids, the effective ϵ is readily obtained from the density of the bulk solid and weight/volume concentration of solids in the bed. As a rule, the materials studied have been nonswelling and the application of the Kozeny-Carman equation has been straightforward.

WET SURFACE AREA

In applying the method to wet pulp in the swollen state as, for example, in water, a considerable amount of liquid is imbibed in the fiber, and contained in the fiber lumen. Since the dimensional swelling of the fibrous mass is not known, the void fraction ϵ cannot be obtained directly from the pad concentration.

To overcome this difficulty we may proceed as follows (*16*). Let the effective volume of the swollen fibers be α cc. per gram of dry fiber. Then at a concentration of c gram per cc., the void fraction becomes

$$\epsilon = 1 - \alpha c$$

Substituting in (4) and using Fowler and Hertel's value of $k = 5.55$ (*15*), we have

$$K = \frac{1}{5.55\ S_0^2} \frac{(1 - \alpha c)^3}{\alpha^2 c^2}$$

It will be noted that $\alpha S_0 = \sigma$, where σ is the external surface area per gram of fibrous material. Transposing the above equation we obtain

$$(Kc^2)^{1/3} = \left(\frac{1}{5.55\sigma^2}\right)^{1/3} (1 - \alpha c) \qquad (5)$$

When permeability measurements are made at several different concentrations of pad material, a plot of $(Kc^2)^{1/3}$ against c yields a straight line when the

Kozeny-Carman equation applies. A typical plot (*16*) is shown in Fig. 1. The specific surface σ is computed from the $c = 0$ intercept. The swollen specific volume α is given as the reciprocal of the $(Kc^2)^{1/3} = 0$ intercept. The consistency corresponding to the latter condition may be envisaged as that to

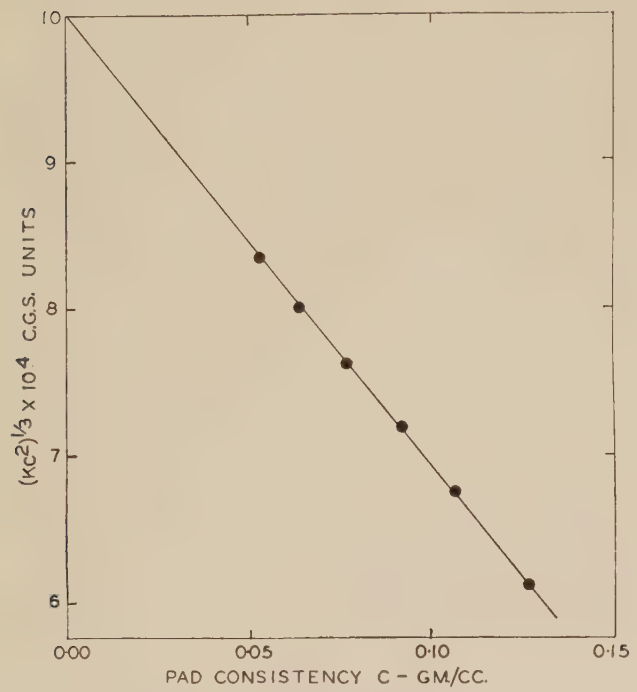

Fig. 1. Modified Kozeny-Carman permeability plot for bleached sulphite pulp (16)

which the system must be compressed, assuming that the fibers are not squeezed out in the process, until the effective solid fraction is unity and the bed is impermeable.

In the experimental method used by the author and co-workers (*16, 17*), a carefully formed pad is confined in a cylindrical permeability cell between two supporting meshes, one or both being attached to a movable piston. This arrangement makes it possible to measure the permeability of a single pad of pulp over a range of consistencies. It has been found that, when precautions are taken to prepare a uniform pad free of occluded air bubbles, and the pad is compressed in such a way that it remains homogeneous, equation (5) applies when the effective solid fraction αc exceeds 0.20, as illustrated in Fig. 2 for a variety of fibrous materials.

The method is by no means free of experimental difficulties. In order to obtain reproducible results it is most important that:

1. The pads be uniform. Flocculation, particularly marked in long-fibered pulps, leads to high values of K.
2. Measurements be made over a reasonably wide range of consistencies in excess of the critical value mentioned above so that the intercepts can be determined by extrapolation.
3. The permeability at a fixed pad concentration remains constant. In many instances there is a tendency for K to decrease with time. Systematic studies (*17, 18*) have shown that the decay is an "end-effect" arising from a partial movement of the fibers at the boundaries of the pad, thus causing a felting. Methods of overcoming this have been devised differing with the type of fiber; but no method, which is generally applicable to all types of fiber, has yet been developed.

The reproducibility of the method on different pads of various cotton and sulfite fibers is illustrated in Table III.

Effect of Beating

The increase of σ various pulps beaten in a Valley laboratory beater was studied (*16*); typical results are shown in Table IV. In these studies, rather limited in scope, it was shown that:

1. The rate of increase of specific surface varies from pulp to pulp and increases progressively with the time of beating. This is in marked contrast to Browning and Baker's observations (*7*) and is illustrated in Fig. 3.
2. The effective specific volume α rises rapidly in the early stages of beating and subsequently appears to level off at a constant value.

The σ values for the unbeaten pulps are of the same order of magnitude as those given by the Clark silvering method, but are considerably higher for beaten stocks.

No systematic correlations could be found between either σ or the rate of development of surface and the strength properties of the sheets. There appears, on the other hand, to be a fairly close correlation between specific surface and the freeness for each type of pulp. Figure 4 shows the freeness plotted as a function of σ for a series of beaten sulphite and kraft pulps of different origins. A similar correlation was found for groundwood pulps.

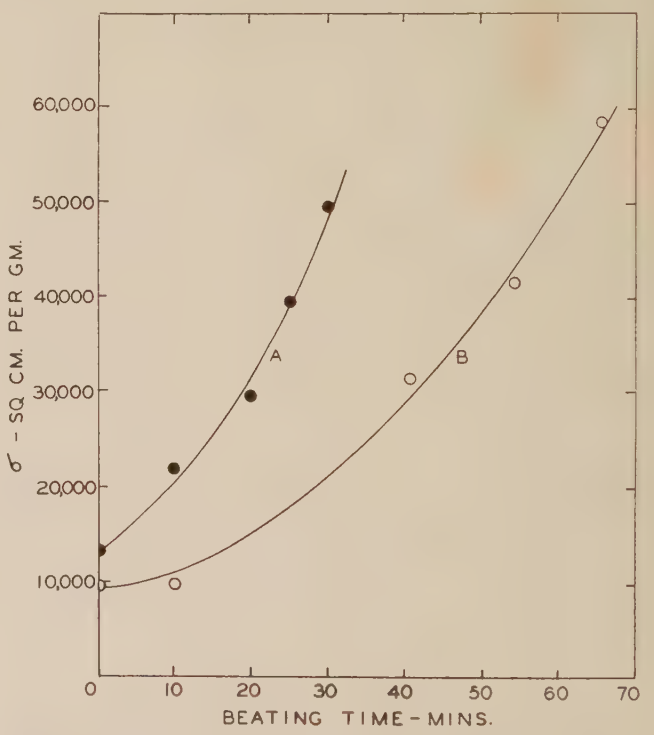

Fig. 2. Range of application to the Kozeny-Carman equation for various fiber-liquid systems

From Robertson and Mason (*16*).

Campbell (*19*) has pointed out that the freeness test is a combined measure of σ and the compressibility of the pulp. The latter property determines the effective void fraction of the pulp layer deposited at the screen in the freeness tester and involves a number of factors, including the average length, length distribution, degree

Table III. Reproducibility of the Water Permeability Method

Material	Consistency range, %	Pad 1	Pad 2	Pad 3	Pad 1	Pad 2	Pad 3	Ref.
		c, sq. cm./g.,			α, cc./g.,			
Sulphite 1— bleached, unbeaten	8 to 14	16,900	16,800	16,800	3.15	3.05	3.30	(16)
Sulphite 2— bleached, unbeaten	8 to 16	14,100	14,500	...	2.50	2.50	...	(17)
Cotton— surgical cotton	14 to 25	5,400	5,300	...	1.30	1.30	...	(17)
Texas standard	14 to 25	5,400	5,800	...	1.20	1.10	...	(17)
Brazilian standard	14 to 25	4,900	5,500	...	1.20	1.10	...	(17)

of swelling, and flexibility of the fibers. The displacement of the three curves shown in Fig. 4 can therefore be attributed to differences in the packing characteristics of the three classes of pulps shown.

The freeness thus emerges as a convenient and rapid empirical measure of the specific surface.

Table IV. The Effect of Beating on the Specific Surface (16)

Sample	Beating time, min.	Freeness (Canadian standard), ml.	α, cc./g.	σ, sq. cm./g.
Sulphite 2 (dried)	0	682	3.13	13,000
	10	515	4.03	21,400
	20	403	4.30	29,300
	25	275	4.60	39,500
	30	178	4.60	49,400
Sulphite 4 (wet)	0	669	4.40	10,200
	7	559	4.90	14,700
	11	498	4.86	19,100
	15	416	5.25	23,400
	18	320	5.12	32,000
	21	242	5.15	38,500
Kraft 2 (wet)	0	738	3.66	9,500
	10	703	4.57	9,700
	41	541	4.70	31,600
	54	429	4.87	41,600
	66	292	4.67	58,400

Since there exists a broad correlation between the specific surface and freeness, it is reasonable, therefore, that the correlation between specific surface and strength properties should be no better than that between freeness and strength. Such was found to be the case.

Effective Fiber Volume

According to the simple theory presented above, α represents the effective "hydrodynamic" volume per gram of fiber—i.e., the volume denied to the flowing liquid. Fowler and Hertel (*15*), using an air permeability method on nonswollen fibrous materials, found that the specific volume value necessary to give results consistent with the permeability method was almost identical with that determined by a gas or a liquid displacement method. For example, an extrapolation of the permeability data on glass wool, similar to that of Fig. 1, yielded an average α value of 0.416 cc./g. compared with 0.414 cc./g. by liquid displacement. The average value of 1.15 cc./g. for a series of water-swollen cottons obtained by Goring and Mason by the permeability method agrees well with 1.10 cc./g. determined by Preston and Nimkar (*20*) by a centrifuging method. The evidence, therefore, suggests that this method of determining the particle volume is fundamentally sound, although the precision is limited by a number of factors, including the uniformity of packing of the pad and end effects, and the range of pad concentrations over which permeability measurements are made.

Brief reference should be made to the α values for sulphite and kraft pulps (Tables I and II). Even allowing for lumen volume, which of course counts as hydrodynamic volume, the α values range from 4 to 9 times the true specific volume of cellulose (0.62 cc./g.), indicating an abnormally high degree of swelling. A portion may be attributed to the action of the fibrils, which might immobilize a portion of the liquid and thus contribute to the effective volume.

An interesting and, it is believed, significant correlation exists between the effective specific volume and the development of strength by beating. This is shown by plotting both the bursting strength and α against the measured σ (Fig. 5). It will be noted that there is a close parallel, especially in the early stages of beating where the major development of strength occurs, between α and the burst factor. Because of inaccuracies in the measured values of α, there is considerable scatter. This type of correlation was found to apply to all beater runs in which strength development was followed.

One is tempted to conclude from these and other results that the real action of the beater in developing strength is not in producing fibrillation and increasing specific surface, but rather in inducing swelling in the fibers by the mechanical action of the beater. This concept of beater action is, of course, not new but it is believed that this is the first experimental evidence supporting this hypothesis. It is possible that the swelling, accompanied by a softening and flexibilization of the fiber, is what the practical papermaker means by the term "hydration" and not the increase in specific surface, as measured in freeness and drainage tests. This increase presumably includes that caused by subdivision of the fiber over and above that resulting from swelling. Until the question of the very high α values is resolved, however, this conclusion should be treated with reserve.

DRY SURFACE AREA

The use of the Kozeny equation in gas flow measurements through porous materials is complicated by a number of factors which do not arise in liquid flow. Allowance must be made for the expansion of the gas as it traverses the bed, causing Q [equation (2)] to increase as the pressure decreases in the downstream direction. Secondly, the gas velocity at the fiber-gas interface is not zero, as implied in the simple Poiseuille equation but, due to "slip," has a finite value which adds to the over-all flow rate. Assuming isothermal flow and a slip factor determined by well-established principles of the kinetic theory of gases,

Rigden (*13*) and Carman (*21*) have shown that the corrected permeability coefficient—i.e., the one to be used in equation (*4*)—has the form:

$$\frac{G}{p} = \frac{K\rho}{\eta L} + B \qquad (6)$$

where

G = mass rate of flow of gas per unit area of bed
ρ = arithmetic mean of entrant and emergent gas densities
B = slip factor

The other symbols are as previously defined.

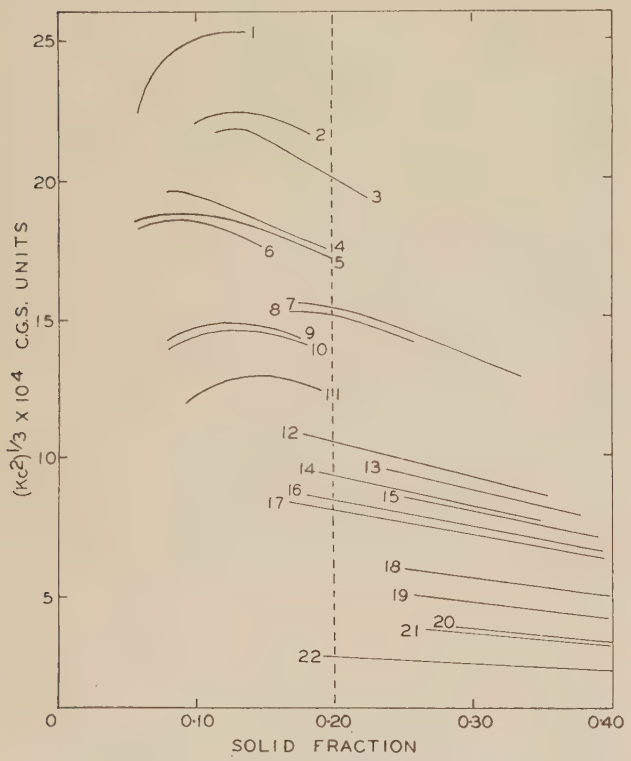

Fig. 3. The development of specific surface by beating in a Valley laboratory beater

Typical examples for a sulphite (A) and a kraft (B) are shown. From Robertson and Mason (*16*).

The correction for slip is most marked at low pressures and low void fractions.

Rigden (*13*) has shown that, when the correction for slip is made, good agreement is shown between the specific surface calculated from the permeability to air and various liquids.

Brown (*22*) has recently published an interesting paper on the application of the air permeability method to pads of loose, unbonded bleached sulphite fibers and handsheets prepared from the same fibers.

Linear plots were obtained when G was plotted against the mean pressure. At atmospheric pressure the slip contributed from 1 to 5% of the total effect, depending upon the void fraction of the sample. The unbonded fiber pads were prepared by the novel technique of freezing them in water, and removing the water by evaporation from the frozen state. Permeability measurements were carried out over a range of concentrations of from 0.15 to 1.2 g. per cc., by applying pressures extending up to 13,000 p.s.i. to a piston in the permeability cell. It is significant that there was none of the decay in permeability experienced with liquids, presumably because of the stiffness of the dry fibers. By making certain assumptions regarding the slip correction, which will not be discussed here, and an ingenious use of both the permeability coefficient K and the slip correction factor B, and furthermore by assuming the specific volume of the fibers to be constant at 0.645 cc. per g., Brown was able to determine the orientation factor $\overline{\cos^2\theta}$ of equation (4). He concluded that $\overline{\cos^2\theta}$ decreases progressively from 1 to 0.25 as the solid fraction increases from zero to 0.37, whereas the factor k_0 remains constant at 3.0.

Table V summarizes Brown's results on the unbonded pads and the handsheets and shows that the bonded fraction of the total area is negligible in the unbeaten sheets and only about 25% in the beaten material. This fraction is considerably less than the values reported by Ratliff (*11*) and is probably closer to the truth, although the criticism of the manner of determining the unbonded area, mentioned earlier, still applies.

Brown's conclusions about the variation of the factor k in equation (4) cast doubt on the validity of the wet measurements on the pulps already discussed since the method of computing σ and α is dependent upon the constancy of k over a limited range of void fractions.

An alternative explanation of Brown's results, based on a constant value of k, is the following. As mentioned above, it was assumed that the effective specific volume of the cellulose is 0.645 cc. per g., the value obtained by helium displacement. Any lumen volume is therefore overlooked. More important, it is conceivable that, when the ice sublimes, the fibers are left in a

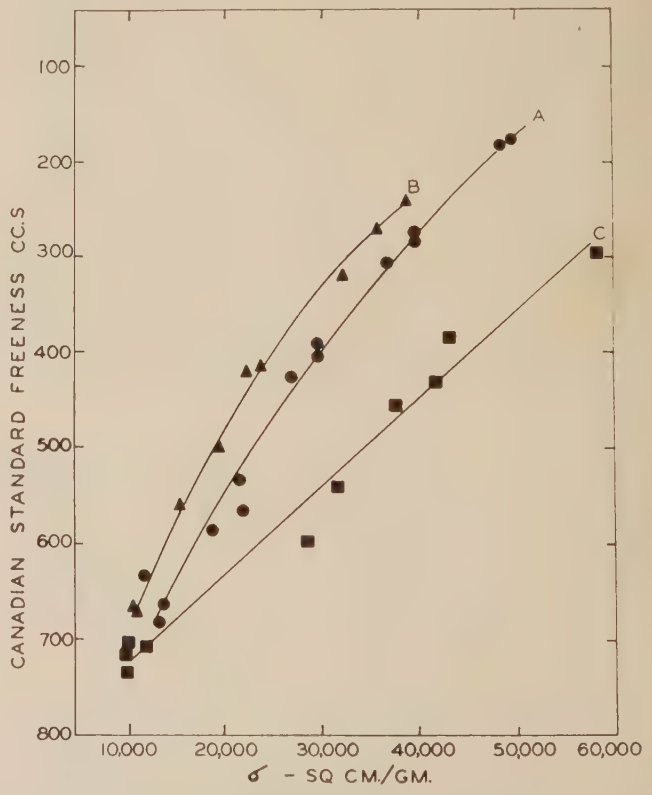

Fig. 4. Correlation between specific surface and freeness for dried (A) and undried (B) bleached sulphite and undried krafts (C) of various origins (16)

Table V. Brown's Specific Surface Measurements (Air Permeability Corrected for Slip)

Pad	σ, sq. cm./g. Unbeaten	σ, sq. cm./g. Beaten to 610 ml. Schopper-Riegler
Unbonded fibers	3800	6750
Handsheet	3800 (approx.)	5000 (approx.)

fluffy or expanded state after the manner of Kistler's cellulose aerogels (*23*), so that α is greater than 0.645 cc. per g. Compression of the bed up to 13,000 p.s.i. subjects the individual fiber to severe deforming stresses, and it is conceivable that, under these conditions, the expanded structure of the fiber collapses with a progressive decrease in α to the true specific volume. Figure 6 shows a $(Kc^2)^{1/3}$ versus c plot of Brown's experimental data. On extrapolation to $(Kc^2)^{1/3} = 0$, corresponding to the application of an infinite pressure, the indicated $\alpha = 0.645$ cc. per g. as anticipated by this explanation. A similar curvature in water permeability measurements at high packing densities has been noted; this is attributed to a compression of the fibers by the confining action of the piston.

DISCUSSION

In the foregoing remarks the emphasis has been placed upon experimental methods, and only selected experimental results have been discussed to illustrate the applicability of each. Each of the three methods possesses certain advantages in application over the other two, but it is clear that none is completely satisfactory. Further, it is clear that discordant results, particularly with beaten pulps, are given by the silvering and liquid permeability methods. The silvering method, while rapid and convenient, is limited to measurements in the water-swollen state and requires improvement in technique, particularly with stocks containing appreciable quantities of fines, before it can be used with confidence. The optical method is rapid if the requisite equipment is available, but suffers from limitations in the theoretical principles involved. Thus far, its main application has been to measurements on pulps in the dry state, although there appears to be no fundamental

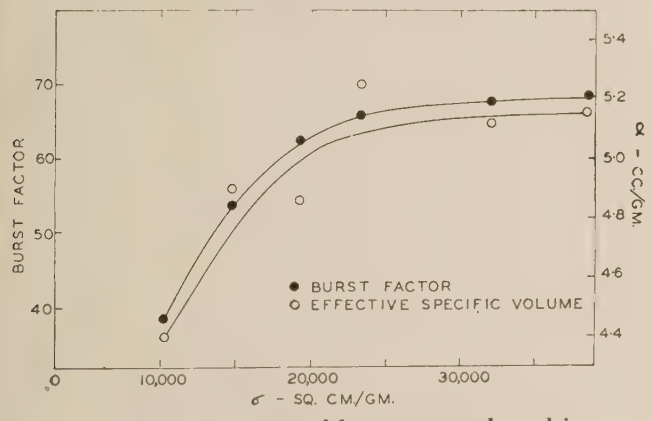

Fig. 5. The development of burst strength and increase of effective specific volume with beating (16)

objection to its application to the wet state. Continued studies of the type reported by Parsons (*10*) and Ratliff (*11*) should add to our understanding of the interfiber relationship in paper. The permeability method appears to offer the greatest scope as it can be applied equally well to bonded and unbonded fiber assemblies in the dry and wet state. In addition, it offers a new method of studying swelling phenomena in fibers, and it is principally this application which interests the author. Considerable improvement in experimental technique and additional verification of the principles involved, however, are necessary before this method can be considered completely reliable.

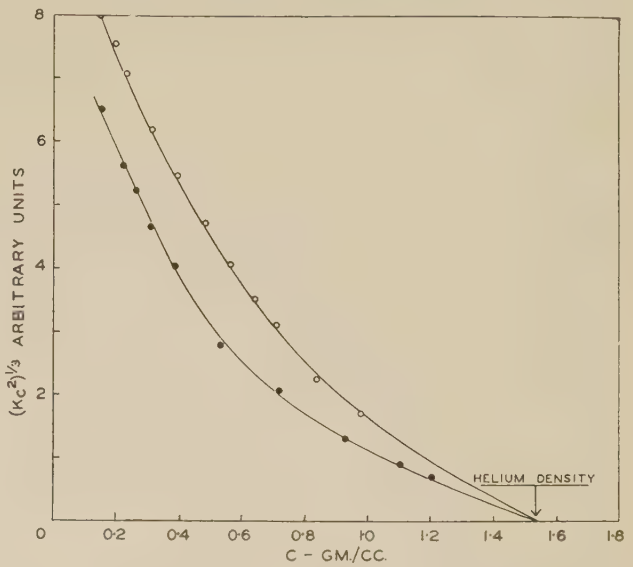

Fig. 6. Modified Kozeny-Carman plot of Brown's (22) air-permeability data on unbeaten (upper curve) and beaten bleached sulphite fibers

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The Specific Surface of Pulps by the Silvering Method

Discussion of the Institute of Paper Chemistry Method of Procedure

B. L. BROWNING

THE SILVERING technique for determining the specific surface area of pulp fibers, which was devised by Clark (*1*), is based upon the catalytic decomposition of hydrogen peroxide at the silvered surface. A further study of the method was made by McEwen (*2*) who prepared the calibration chart which is still in use.

Although the Clark-McEwen method was fairly successful in testing unbeaten fibers, the subsequent application to pulps which were rather highly beaten led to unsatisfactory results at both the Canadian Forest Products Laboratories (*3*) and The Institute of Paper Chemistry. Certain modifications of the method, which were found necessary in testing beaten pulps, have been described by Browning and Baker (*4*).

The method given below differs in some minor details from those previously described and represents the procedure now in use at The Institute of Paper Chemistry.

METHOD OF TEST

Apparatus

1. The reaction apparatus designed by Clark and shown in Fig. 1 of TAPPI method T 226 sm-46 (*5*) is used. It is important that the direction of rotation of the propeller be such as to cause a downward deflection of the liquid as it flows past the indentations in the reaction flask.
2. Two hot plates (1200-watt, three-heat). One is set at "medium" for silvering fibers. A motor-driven, small glass propeller is mounted above the plate. The propeller is adjusted to approximately 350 r.p.m. The second hot plate is set at "high" for the initial heating.
3. Jena (1G1) crucibles or Pyrex fritted glass crucibles of coarse porosity.
4. Porcelain casserole of approximately 210-ml. capacity.
5. Rubber policeman.
6. Stopwatch or stopclock, preferably 100 seconds per revolution.
7. Steel dissecting needle.

Reagents

1. Silvering solution. Dissolve 200 grams of C.P. silver nitrate in 1500 ml. of water. Add, with stirring, 160 ml. of concentrated ammonium hydroxide. Then slowly add dilute ammonium hydroxide (1:10) until the brown precipitate first formed *just disappears, avoiding addition of an excess.* Dilute with water to 2 liters and store in a dark glass-stoppered bottle. This solution may be kept for periods up to one month.

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2. Potassium permanganate, 0.5 *N*. Weigh out 31.6 grams of C.P. potassium permanganate and dissolve in about 1.5 liters of water. Treat the solution by any of the generally accepted procedures to remove manganese dioxide, filter through asbestos, and dilute to 2 liters. This solution need not be accurately standardized.
3. Hydrogen peroxide, 0.5 *N*. Measure 25 ml. of 30% hydrogen peroxide into about 750 ml. of water containing 4 ml. of *N* sulphuric acid. Dilute to approximately 1 liter. Adjust the concentration so that 24.5 to 25.0 ml. of hydrogen peroxide solution is equivalent to 25.0 ml. of potassium permanaganate solution. This adjustment must be made daily.
4. Sulphuric acid, 2 *N* (approximate). Dilute 53 ml. of concentrated sulphuric acid to 1 liter.
5. Sodium borate buffer solution. Weigh out 25 grams of C.P. sodium borate ($Na_2B_4O_7.1OH_2O$) and add it to 400 ml. of warm water containing 20 ml. of *N* sodium hydroxide solution. Dilute to 500 ml. Dilute 100 ml. of this solution to 2 liters.
6. Asbestos. Ordinary acid-washed asbestos of Gooch crucible grade made into a slurry with water to a consistency suitable for Gooch crucible preparation (approximately 3 grams of asbestos per 100 ml.).

Procedure

If the pulp is dry, weigh out several grams and completely defiber in distilled water with a minimum amount of agitation and stirring. If the sample is received in slush form, the preliminary defibering procedure is unnecessary.

Filter an amount of the pulp suspension equivalent to approximately 1 gram of oven-dry pulp through a coarse-porosity, fritted glass crucible (do not apply suction until a mat is formed), and wash thoroughly with distilled water. Remove the pulp pad from the crucible with the dissecting needle, and place all or a portion of it in a 4-liter beaker.

Add enough distilled water to give a consistency such that a 110 to 150-ml. portion will require 3 to 8 ml. of potassium permanganate in the back titration. The proper consistency must be determined by making a preliminary specific surface determination following the procedure outlined below. It is usually preferable to have a volume of 2 to 3 liters at this point, and to achieve any further adjustment of the concentration by the amount of wet pulp added.

Table I may be used as a guide in estimating the approximate size of sample to be taken.

Using the porcelain casserole, vigorously agitate the suspension, then quickly remove a portion of not less than 110 or more than 150 ml. by dipping the casserole to the bottom of the beaker and lifting it out. Transfer the entire portion to a graduate and record the volume

to the nearest milliliter. Pour the sample into a 250-ml. beaker, rinsing the graduate with a few milliliters of water. Heat to boiling by placing the beaker on the hot plate set at "high." When the liquid is boiling, add 16 ml. of silvering solution from a Mohr pipet and place the beaker on the second hot plate set at "medium." The temperature of the solution during the silvering operation should be very close to 100°C. The motor-driven stirrer is immediately started rotating in the solution at about 350 r.p.m. Note the time at the beginning of the stirring.

Table I

Pulp	*Approximate area, sq. cm./g.*	*Desired consistency, g. of oven-dry pulp/l.*
Unbeaten pulp	7000–15000	0.15–0.25
Groundwood	15000–25000	0.12–0.15
Beaten pulp	10000–40000	0.10–0.20
Headbox stock	20000–100000	0.03–0.10

After a total silvering period equivalent to three times that from the beginning of stirring to the change in color of the fibers from reddish-brown to black, remove the beaker from the hot plate, add about 10 ml. of asbestos suspension, stir, and filter immediately on a Gooch crucible containing a $^1/_8$-inch asbestos mat. Rinse the beaker with water, and with a rubber policeman push any fibers clinging to the sides of the crucible to the bottom. Add to the crucible an additional 10 ml. of asbestos suspension to form a mat on the fibers. Wash thoroughly with distilled water, taking care to wash all soluble silver salts from the inside wall of the crucible.

When the washing is complete, remove the mat together with all silvered fibers to the reaction flask with the dissecting needle. Attach the flask to the stand and add 100 ml. of the diluted buffer solution that has been adjusted to 20 to 21°C. (If the temperature of the laboratory is considerably removed from 20°C., it is desirable to control the temperature during the reaction by placing the reaction flask in a pan of water adjusted to approximately 20° C.) Run into the special funnel a volume of hydrogen peroxide equivalent to 25.0 ml. of potassium permanganate. Turn on the stirrer, which has been adjusted to rotate at 600 r.p.m. Open the funnel stopcock and start the timer at the moment the peroxide enters the solution. Rinse the funnel with 2 to 3 ml. of water. At the end of 20 seconds, record the temperature and remove the thermometer to prevent accumulation of fibers against it. Close the funnel stopcock and place 15 ml. of 2 *N* sulphuric acid in the funnel.

At the end of exactly 100 seconds, run the sulphuric acid from the funnel into the reaction flask and rinse the funnel with water.

Titrate the remaining undecomposed hydrogen peroxide with potassium permanganate. From the number of milliliters of potassium permanganate used, determine the surface area of the sample from the calibration curve (TAPPI Method T 226 sm-46).

If the consistency of the suspension is either too low or too high, as indicated by the permanganate titration, it must be adjusted and the above procedure repeated until the desired consistency is obtained.

The consistency is determined by filtering off the fibers contained in 500 ml. of suspension on a Gooch crucible with an asbestos mat, drying at 105°C., and weighing. The consistency sample is measured with the same care used in measuring the test specimen. The pulp suspension is thoroughly stirred, portions are dipped out with the casserole, and the whole of each portion is transferred to a 500-ml. graduated cylinder. The volume is made up to 500 ml. by dipping out small portions for the final adjustment. The consistency is run in duplicate.

$$\text{Weight of fibers} \times 2 = \text{consistency (g./l.)}$$

$$\text{The specific surface of the pulp} = \frac{\text{Surface area of sample} \times 1000}{\text{Milliliters of sample} \times \text{consistency of sample}}$$

Run at least three determinations and report the mean. The maximum deviation should not exceed $\pm 5\%$ of the mean.

Notes

1. Between determinations, the reaction flask, propeller, funnel, and thermometer should be rinsed thoroughly with distilled water. To remove deposited material from the reaction flask, treat with hot cleaning solution (20 grams of potassium dichromate in 300 ml. of concentrated sulphuric acid).

2. When the hydrogen peroxide buret does not drain cleanly, it is necessary to treat it with 50% sodium hydroxide solution, afterward washing it thoroughly with distilled water.

3. The silvering beakers must be washed occasionally with concentrated nitric acid to remove deposited silver.

4. The time required for silvering depends upon the nature of the pulp, and may vary from 5 to 60 minutes. In case of doubt, or in testing a pulp of unusual character, it is recommended that several samples be run at different silvering times. The results obtained when silvering is continued beyond a certain minimum time will be found essentially identical. Microscopic examination of a few fibers removed from the suspension with a dissecting needle will be found helpful in judging the course of silvering. The time of silvering, beyond the minimum necessary to completely cover the fibers with a black coating of silver, is not critical. Excessive silvering times result in a slow increase in area, caused by actual changes in dimensions of the silvered fibers, and should be avoided. Also, the fibers may become brittle and break into fine fragments during the stirring.

DISCUSSION

Comments on the Revised Method

The modifications of the method as originally described by Clark and McEwen are chiefly those which have been found necessary in the testing of beaten pulps.

The preliminary washing of the pulp with distilled water is desirable because certain pulps contain soluble materials which may influence the test by affecting the catalytic action of the silver surface, or by forming a debris of reduced silver which markedly alters the results.

It has been found preferable to silver and test a whole

aliquot of the original fiber suspension. It is difficult to secure reliable aliquots of the silvered fibers.

The filtration of both the consistency sample and the silvered specimen on Gooch crucibles with asbestos mats was found necessary to completely retain fine particles when dealing with well-beaten pulps. The addition of an asbestos suspension to the silvered fiber suspension before filtration was found advisable to prevent the clumping and compacting of the fibers. These clumps, in the case of well-beaten pulps, were found not to disperse readily during the later peroxide decomposition reaction*. No "blank" on the asbestos fibers has been observed, although the possibility of some secondary effects, such as that of liquid movement during the peroxide decomposition reaction, has not been excluded.

The revised method is readily carried out; it gives results of satisfactory precision on a single specimen, and it gives reasonably consistent values through a series of changes—e.g., beating.

Comments on the Silvering Procedure for Determining Surface Area

There are a number of possible errors in the method, several of which have already been pointed out by Mason (*6*). We do not know the absolute accuracy of the specific surface determination by the silvering technique. Although the calibration curve was prepared from measurements made on silvered cellophane, the area of which could be measured in a fairly reliable manner, we do not have complete assurance that changes in contour of the silvered surface would be without effect. Also, we do not know to what extent the silver surface is uniformly catalytically active. There seem to be some indications, including some in Clark's original work, that all silver surfaces do not have the same catalytic activity.

Because the effective reaction of peroxide decomposition occurs at a surface, the relative motion of surface and liquid is important. Thus, the rate of stirring during the reaction has a very important effect. Further, these considerations suggest caution in accepting unqualifiedly the calibration curves derived on cellophane squares when applied to pulp fibers.

The procedure of hot silvering must be subjected to a rather critical examination, because it is known that heating of a hydrated pulp to 100°C. destroys much of the hydration as measured by freeness. If, as might be expected, a similar change occurs on heating for the silvering step, it may be that we are changing the property we are trying to measure in the process of measuring it. Clark and others have attempted to apply cold silvering techniques, but without success as yet.

Comments on the General Problem of Surface Area Measurement

It is axiomatic that a property must be defined before it can be measured in a satisfactory manner (*7*). In surface-area measurements, there is as yet no adequate definition of the property it is sought to evaluate. Thus, microscopic measurements, the silvering method, permeability methods, and adsorption methods do not give the same results, yet all may be correct. This is not surprising, because the extent to which the property is measured may depend upon the method of measurement. For example, in the microscopic method, all the very fine contours in an irregular surface are not measured, whereas these are probably measured in the silvering method if they are not too fine. Similarly, irregularities of a still smaller degree of magnitude are probably not measured by the silvering method, because the silver coating tends to level out the depressions, whereas they may be measured by a molecular adsorption method. It seems likely that the results of permeability methods fall somewhere between the extremes of the other methods listed above.

The problem, then, is to define the kind of surface which is of interest. It is quite possible that the most suitable type of definition depends upon the correlated property with which a relationship is sought. To cite one specific example, it seems certain that the bonded area in a paper sheet is, to some extent, a function of the surface area of the pulp developed by beating. However, the type of surface which is effective in bonding may be that which is determined by one specific method only.

The problems of "fines" in well-beaten pulps is an extremely important one. The earlier application of the silvering method to beaten pulps showed that a considerable part of the total surface area was represented by the very fine material, and that this material was partially lost in the test unless the procedure was modified.

The difficulties in measurement because of the presence of fines is not wholly obviated when the permeability method is used, as Mason has found some redistribution in the material of the bed during the flow test.

It is necessary to consider the effect of these very fine fractions on the physical properties of sheets made from the fibers and the relationship of these properties to the surface area measurement. That is, it should be determined whether the contribution of the fines to the specific surface is represented by corresponding increments in the properties of the paper sheets.

* In the testing of some well-beaten pulps, the silvered fibers and particles agglomerate and roll into small lumps before the silvering is completed. When this occurs, the lumps are not broken up during the subsequent peroxide decomposition reaction and the results of the test are valueless. Since no way has been found of overcoming the difficulty, the method cannot be recommended for pulp specimens in which clumping occurs during silvering.

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The Electrokinetic Properties of Cellulose Fibers

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Certain modes of behavior of papermaking fibers are often attributed to the effect of the charge of the electrical double layer, by analogy with the classical theories of colloid stability. Such explanations should be employed with caution. The methods of measuring the zeta-potential of cellulose fibers by streaming and electro-osmosis are discussed and it is shown that, on the grounds of faulty experimental methods and of limitations in the electrokinetic theory of fibers, the significance of the reported data in the literature is doubtful. Unlike many systems, the origin of the electrical charge in cellulose fibers is obscure. The possible application of electrokinetic measurements to the study of the dimensions of surface layers is briefly discussed.

THE organizing committee of this symposium has indicated a desire that not only should a summary of the "present status of our knowledge" of the various topics under discussion be presented, but also that "specific gaps in our knowledge be emphasized." Unfortunately, the relation between the electrokinetic and papermaking characteristics of pulp fibers consists almost entirely of gaps.

The electrokinetic phenomena—i.e., cataphoresis, electro-osmosis, stream current and potential, sedimentation potential, surface electrical conductance, and the electroviscous effect—have played an important role in the development of colloid science, particularly in what we might call its classical phase. The fundamental quantity of electrokinetics is the "zeta-potential" which, in the beginning, was considered to be of a simple and straight-forward nature, but has since been the center of considerable controversy. In spite of over-simplification, the zeta-potential concept has nevertheless served to explain many phenomena in colloidal systems, such as peptization and coagulation of sols, swelling of lyophilic materials (proteins), etc. The stability of a sol, for example, is attributed in part to the mutual repulsion of the particles by electrical forces which come into play when the electrical double layers surrounding the particles interpenetrate one another. When the zeta-potential falls below a critical value, the long-range London-van der Waals attractive forces come into play and the system coagulates.

Although the significance of the zeta-potential is now recognized to be much more complex than hitherto regarded (*1*) even in simple lyophobic colloids, it is natural that the paper chemist should try to explain many of the colloidal properties of papermaking stocks in terms of the electrical charge in the same manner as, for example, the protein chemist has been able to do, often with spectacular success, in the systems with which he is concerned. Thus one finds scattered through the literature "explanations" of such phenomena as fiber-fiber flocculation, pitch deposition, the retention of various colloidal additives as in wet-strengthening, sizing, dyeing, etc., based upon the electrical interaction of the cellulose fibers and other particles. It must be emphasized at the outset, however, that the thread of experimental evidence upon which these explanations hang is very tenuous, and the explanations are, at best, only qualitative. Numerous investigations of the zeta-potential of cellulose have been carried out. The results with several recent exceptions (*2–6*) have already been reviewed in detail (*7–9*). As this paper will attempt to show, the significance of most of the published data is uncertain, partly because of faulty experimental methods, but mainly because of an over-simplification of the meaning of zeta-potential as applied to a swollen cellulose fiber.

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THE ELECTROKINETIC EQUATIONS

A solid in contact with a polar liquid acquires an electrical charge by various mechanisms, the most important of which are the yielding of mobile ions of one sign to the liquid (as in metals and proteins), and the adsorption from the liquid of cations or anions having a specific affinity for the solid. The excess charge of opposite sign accumulates as a diffuse ionic layer of "gegenions" (the Gouy-Chapman layer) in the liquid adjacent to the solid, and is distributed in accordance with the Poisson-Boltzman equation. This mobile charge leads to the electrokinetic phenomena which can be used to measure the difference in potential between the surface of the solid and the bulk liquid. The quantity so measured is known as the zeta-potential.

Table I. List of Symbols

A	=	cross-sectional area of pad
a	=	cross-sectional area of a pore
c	=	concentration of solids in pad (mass/volume)
D	=	dielectric constant of liquid
E	=	potential difference across pad causing electro-osmosis
F	=	volume rate of electro-osmotic flow (zero external hydraulic resistance)
I	=	stream current (zero external electrical resistance)
K	=	permeability coefficient of pad
L	=	thickness of pad
p	=	pressure drop across pad which causes streaming
R	=	electrical resistance of pad
V	=	stream potential (infinite external electrical resistance)
α	=	effective swollen specific volume of fibers
σ	=	equivalent thickness of diffuse ionic layer
ϵ	=	effective void fraction of pad
ζ	=	zeta-potential
η	=	viscosity of liquid
θ	=	angle between direction of a pore and axis of a cylindrical pad
κ	=	specific conductivity of liquid
μ	=	ionic strength
ξ	=	pore factor

Cellulose fibers in contact with water and dilute electrolytes acquire a negative charge. In the methods which have been used to measure the zeta-potential of cellulose, apart from cataphoresis which is limited to

studies of fiber fragments (*3, 10*) and is not considered further, the principle is as follows. A uniform cylindrical pad of fibers is held in position between two perforated electrodes. When an electrical potential is applied across the system, the mobile charge in the liquid migrates toward one electrode, dragging the bulk liquid with it. The resulting flow is called electro-osmosis. If, alternatively, the liquid is caused to flow through the pad by the application of a pressure gradient, a flow of electrical charge occurs. The stream current thus generated can be measured by passing it through a low-resistance galvanometer. If no charge is withdrawn from the system and the stream current leaks back through the pad, a potential difference is established across the pad. This is known as the stream potential and is related to the current and the resistance of the pad by Ohm's law.

The relationship between these three observable quantities is given by the well-known Helmholtz-Smoluchowski equations.

$$I/p = V/pR = F/E = \frac{D\zeta}{4\pi\eta L}\xi; \qquad (1a)$$

the symbols are defined in Table I. The quantity ξ (*3*) is determined by the internal network of pores in the pad and is known as the pore factor. It can be written in the form

$$\xi = \sum a \cos\theta = \frac{A\epsilon}{2}, \qquad (1b)$$

where the summation extends over all pores. Equations (1) are expressed in different ways by different authors but, basically, they are all equivalent and differ only in the value in the denominator of the last term of equation (1b); this depends upon the distribution function of pore orientations assumed. As will be seen later, any uncertainties about this factor, provided it can be considered to be the same for all pads, are of little consequence in comparison with other inperfections in the theory.

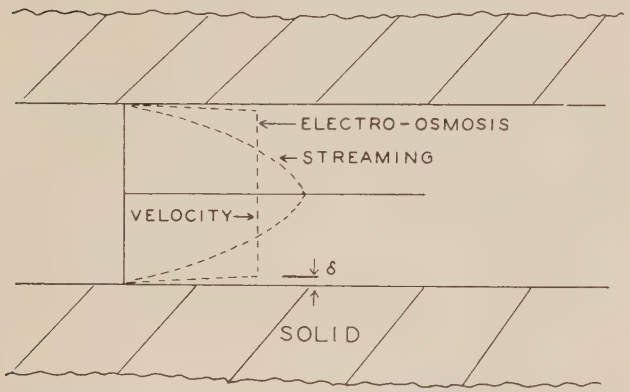

Fig. 1. Velocity profiles in a circular capillary in streaming (Poiseuille-type flow) and electro-osmosis

These relations are based on a number of assumptions whose limitations are often overlooked. The most important of these (*5*) are the following:

1. The solid surface is flat and only the external fiber surfaces are involved.
2. The electrical potential of the solid surface, relative to the bulk liquid, is constant over the entire surface—i.e., each portion of all fibers is "electrokinetically" identical.
3. In streaming, the flow is laminar and the entire space charge at any point in the liquid moves with the same velocity as the liquid at that point.
4. In electro-osmosis, the electrical force of the external field acting on the space charge is balanced by the viscous force of the liquid.
5. The velocity gradient, or shear rate, at the envelope of zero liquid velocity—i.e., at what we have previously (1a) referred to as the "hydrodynamic surface" of the particles—is constant throughout the bed.
6. The internal pore network is statistically uniform throughout the pad.

These assumptions obviously impose a number of serious limitations upon the interpretation of the experimental data.

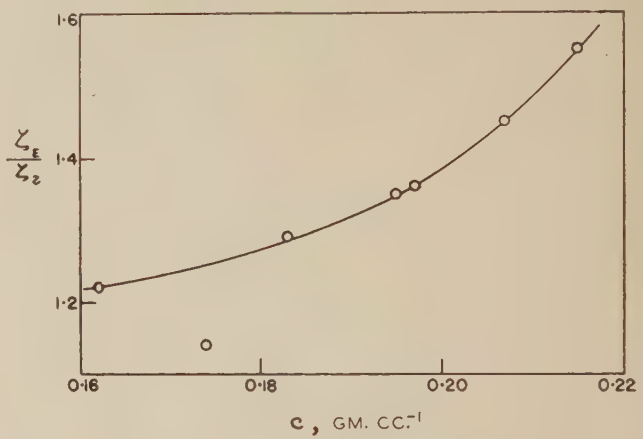

Fig. 2. Comparison of ζ of cotton in distilled water by streaming and electro-osmosis

From Goring and Mason (*5*).

As was first clearly pointed out by Stern (*11*), ζ is the electrical potential, relative to the bulk liquid, at the surface of zero liquid velocity. This potential is not necessarily equal to the electrochemical potential of the bulk solid.

The pattern of flow in stream measurements is radically different from that in electro-osmosis. For example, in streaming through a circular capillary, the velocity profile is parabolic; on the other hand, in electro-osmosis, flow is of the plug type—i.e., the velocity is constant across the capillary except very close to the walls where the entire velocity gradient is concentrated (Fig. 1). Agreement between the two methods, therefore, can be expected only if hydrodynamic surfaces are identical in both cases. Excellent agreement has recently been found for single glass capillaries of various sizes (*12*). The only comparisons which have been reported on cellulose fibers are those of Goring and Mason (*5*) for a series of cotton pads of different concentration. The results, shown in Fig. 2, indicate a discrepancy which increases at high pad concentrations.

In applying equation (1a) to calculate ζ, it is necessary to evaluate the pore factor, ξ, and it is here that the real trouble begins.

In the classical Helmholtz-Smoluchowski method, the electrical conductance is taken as that of the liquid

in the pores. Assuming Ohm's law, this leads to

$$\xi = L/\kappa R \qquad (2)$$

where κ is the bulk conductivity of the bulk liquid. Thus, for example, the stream potential becomes

$$V = \frac{D\zeta}{4\pi\eta\kappa} p, \qquad (3)$$

indicating the stream potential to be independent of the dimensions and condition of packing of the pad.

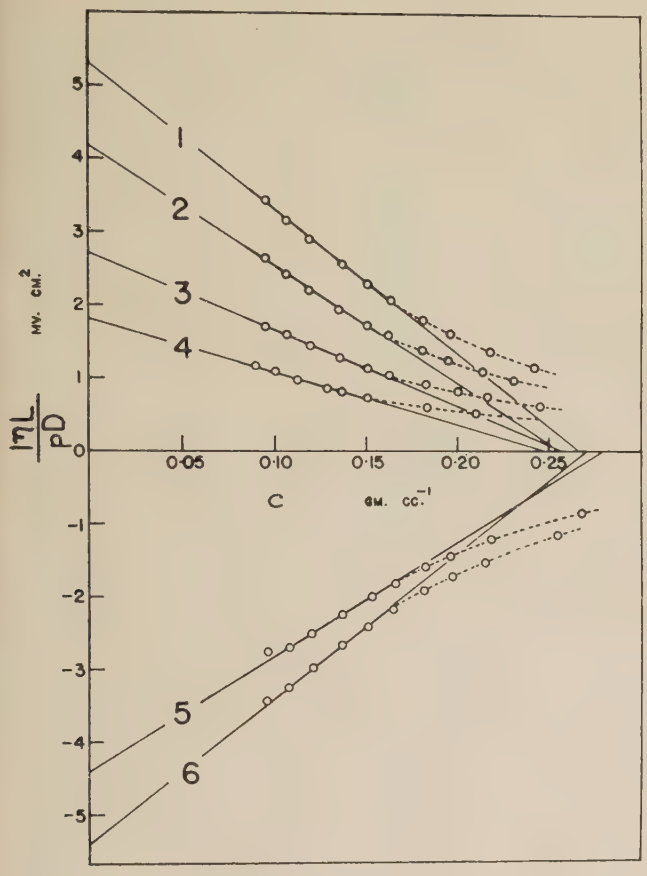

Fig. 3. Stream current plots for pads of sulphite pulp at different concentrations of KCl (curves 1, 2, and 3) and $ThCl_4$ (curves 4, 5, and 6)

From Goring and Mason (*6*).

Equation (3) is widely quoted in textbooks dealing with electrokinetic phenomena but is invalidated by a number of effects. One of these is surface electrical conductance which owes its origin in part, at least, to the electro-osmotic transfer of current over and above ordinary electrolytic conductance. Thus equation (2) yields a value of ξ which is too high. To overcome this complication Briggs (*13*) carried out stream-potential measurements, then replaced the electrolyte with one of high concentration, in which the surface conductance was presumed to be a negligible part of the whole, and determined ξ from equation (2). The Briggs stream-potential method has been the source of most of the zeta-potential data on cellulose fibers reported in the literature.

There are, however, two additional complications in cellulose systems which Briggs failed to take into account. Bikerman (*14*) has pointed out that, in pads composed of swollen gels, the paths for ionic transfer and fluid flow are unlikely to be identical as implied in equation (2). Appreciable quantities of electricity can flow through, as well as around, the fibers. It has since been confirmed experimentally that the Briggs procedure is fundamentally unsound (*5*).

A second but less serious complication arises from an ultralow frequency dispersion of electrical resistance recently noted in pulp fibers (*15*). Here decreases of up to 30% in the electrical resistance between d.c. and 100 c.p.s. can occur. The amount of dispersion appears to increase with the amount of swelling, and is sensitive to changes in the zeta-potential. Reversal of the charge on sulphite pulp by addition of thorium ions, for example, can destroy the effect. In the Briggs method, the resistance was usually measured at 1 kc., whereas the quantity appearing in equation (1a) is the d.c. value; this introduces an unknown and variable error.

It is of interest to note, in passing, that the two effects mentioned above can complicate the interpretation of measurements of the "surface conductance" of cellulose (*2, 16, 17*). A discussion of this aspect of electrokinetic phenomena is, however, beyond the scope of this paper.

Neale and Peters (*4, 18*) overcame these objections by measuring the stream current collected on non-polarizing (reversible) electrodes and calculating the void fraction directly from the pad concentration. This procedure avoids using the electrical resistance of the pad in the calculations, and no assumptions about the mechanism of electrical conduction are necessary. Although it is not specially stated, it appears that the unswollen specific volume was used. It was found that ζ decreased with increasing pad concentration. However, by standardizing the pad concentration, relative values for a given species of fiber were obtained in the presence of various electrolytes. Their results for a number of natural and synthetic textile fibers, including cotton and rayon, are probably the most reliable in the literature.

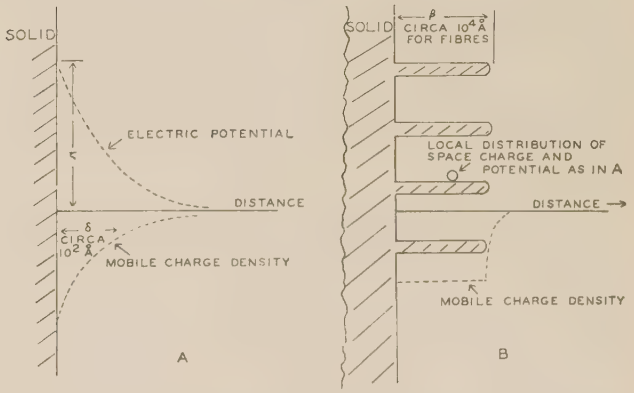

Fig. 4. Diffuse double layer according to conventional theory for a flat surface (A) and proposed theory for a swollen polymer (B) (schematic)

Goring and Mason (*6*) have extended this method to take dimensional swelling into account. If α is the effective specific volume of the swollen fibers, $\epsilon = 1 - \alpha c$ and the stream current in equations (1) becomes

$$\frac{I\eta L}{pD} = \frac{A\zeta}{8\pi}(1 - \alpha c) \qquad (4)$$

By measuring the stream-current function $I\eta L/pD$ at different pad concentrations, ζ and α can be computed by a method of intercepts similar to that employed with the Kozeny-Carman permeability equation (*19*). It follows from the theoretical principles embodied in equation (4) that the values of α obtained from permeability and stream-current measurements should be identical.

Figure 3 shows a set of curves for different pads of a bleached sulphite pulp at several concentrations of KCl and $ThCl_4$ on both sides of the neutral point. The lines are straight, except at high concentrations where deviations from linearity occur, paralleling those of the permeability function $(Kc^2)^{1/3}$ previously discussed (*19*). This curvature is attributed to a distortion of the fibers by compression of the pad; it did not occur with cotton pads. The intercepts (Fig. 3) are independent of the value of the zeta-potential. However, the values of α were consistently higher than those obtained by the permeability method (Table II). Since the latter values are believed to represent the correct values, at least in the case of cotton if not with the sulphite fibers, a serious defect in the electrokinetic theory is indicated.

The explanation for this discrepancy is as follows. The distribution of ions in the liquid layer adjacent to the solid can be computed from the Poisson-Boltzman distribution. For a flat surface, the space-charge density decreases with the distance from the surface in a roughly exponential manner as is indicated in Fig. 4A. The gradient is determined by the ionic strength of the electrolyte.

A convenient method of expressing the distance over which the charge is distributed is to compute the position of the center of gravity of the free charge. This distance is known as the equivalent layer thickness and is given by the relation

$$\delta = \frac{B}{\sqrt{\mu}} \qquad (5)$$

where B is a calculable constant. Table III gives values of δ for KCl solutions and indicates them to be very small, particularly in relation to the length of a cellulose molecule. And yet electrokinetic effects rise almost entirely in this exceedingly thin layer. It is doubtful, therefore, if the model of a flat solid surface—i.e., flat within a few A.—is applicable to any material (*14*) and especially to swollen cellulose.

An alternative, and highly simplified, model of the cellulose/liquid interface has been tentatively adopted to explain the results. This model (Fig. 4B) is a simple extension of the partial solution theory originally advanced by Campbell (*20*). The surface molecules of swollen amorphous cellulose are considered to be anchored to the solid with a portion of the molecule or a group of molecules "dissolved" and free to move in a restricted Brownian movement. These groups are long compared with the double layer thickness, and bear an electrical charge. Each such group is surrounded by its own Gouy-Chapman diffuse double layer. In streaming and electro-osmosis, only the free space charge in each layer is capable of movement since the partially dissolved chains are restrained.

It is obvious that, in such a system, streaming and electro-osmosis are much more complicated phenomena than pictured by the conventional theory based on a flat surface. Goring and Mason (*6*) have shown that this model accounts for the discrepancy in α, and that an order of magnitude of the length β of the chains is 15,000 to 20,000 A. Since this corresponds to chains containing 3000 to 4000 anhydroglucose units, it is perhaps questionable to call these molecules. Fibrils of this length, however, are clearly discernible in electron-microscope images of the surface of unswollen fibers. Thus the order of magnitude of B calculated from the stream-current data is reasonable.

On the other hand, this model of the interface does not account for the observed discrepancy in the ratio of ζ streaming/ζ electro-osmosis. It is possible that this failure of the models is due to over-simplification.

Table II. Comparison of Swollen Volumes by Electrokinetic and Permeability Methods (6)

Type of cellulose	*Permeant*	*ζ, mv.*	*α From stream measurement, cc./g.*	*α From permeability measurement*
Surgical cotton	10^{-4} *N* KCl	−32.5	1.60	1.30
Texas cotton	10^{-4} *N* KCl	−31.4	1.70	1.20
Brazilian cotton	10^{-4} *N* KCl	−30.5	1.70	1.10
Mexican cotton	10^{-4} *N* KCl	−25.8	1.40	1.00
Bleached sulphite	2.5×10^{-5} *N* KCl	−22.8	3.70	2.50
Bleached sulphite	10^{-4} *N* KCl	−26.2	3.70	2.50
Bleached sulphite	10^{-3} *N* KCl	−20.2	3.90	2.50
Bleached sulphite	5×10^{-3} *N* KCl	−13.2	3.90	2.50
Bleached sulphite	2×10^{-2} *N* KCl	−8.8	4.00	2.30
Bleached sulphite	1.4×10^{-4} *N* $ThCl_4$	+21.5	3.70	2.50
Bleached sulphite	2.1×10^{-4} *N* $ThCl_4$	+26.4	3.70	2.50

Table III. Equivalent Thickness of Gouy-Chapman Diffuse Layer

KCl, N	*δ, a.*
10^{-5}	900
10^{-4}	300
10^{-3}	100
10^{-2}	30

Whether or not this is the correct explanation, or whether the discrepancy can be attributed merely to surface roughness, as suggested by Bikerman (*14*) or to unknown complications of the flow equations resulting from the shapes and orientations of the pore network, it is obvious that the physical meaning of the quantity ζ computed from the conventional equations differs from that indicated by the flat interface theory. It is difficult to assign any particular meaning to ζ other than that it is proportional to the amount of mobile charge. It is clear, however, that ζ is less than the potential of the bulk solid.

ORIGIN OF ELECTRICAL CHARGE

Thus far nothing has been said about the origin of the electrical charge in cellulose. Indeed this is obscure, except for evidence in many instances that it is determined in part by preferential adsorption of cations (Al^{+++}, Th^{++++}, cationic dyes, etc.) or anions (Cl^-, anionic dyes, etc.) The adsorption phenomena are complex and, as with other surface active solids, cannot be predicted in advance except that adsorption of heavy ions is generally favored.

The source of the negative charge in pure water remains an open question. The zeta-potential is fairly sensitive to changes in pH and passes through an isoelectric point at pH 2.5 (*4*, *21*) although, as Stamm points out (*7*), this value may be meaningless because of possible hydrolysis of the cellulose at this acidity. From the marked effect of pH it may perhaps be concluded, by analogy with other systems such as proteins, that the charge originates by loss of protons from active hydroxyl or occasional carboxyl groups in the cellulose. On the other hand, Neale and Peters' (*4*) observations of the variation of ζ with pH cannot be accounted for quantitatively by the dissociation hypothesis. Since, however, the absolute magnitude of ζ enters into the calculation, the calculation may be invalidated by the experimental data. Some support is added to the hypothesis that pure cellulose is not ionogenic by the observation (*2*, *4*) that the introduction of carboxyl groups by oxidation leads to a decrease rather than an increase in the negative potential.

Neale and Peters (*4*) point out that most chemical neutral (nonionogenic) solids acquire a negative charge in contact with water and conclude that this is due to an intrinsic property of water to expel electrons from itself.

When the fibers contain ionogenic groups (such as lignosulphonates) and other base-exchange constituents, the electrokinetic characteristics may be profoundly modified. No electrokinetic studies, however, have been carried out on commercial pulps in spite of their potential interest in this connection. It should be borne in mind that, if macromolecules in the interior of the swollen fiber are ionized, a Donnan-type of membrane equilibrium will be established with electrical potential gradients established internally. This will further complicate the interpretation of ζ; this complication applies to all swollen ionogenic materials.

CONCLUSION

It is evident from the foregoing discussion that the electrokinetic phenomena in cellulose fiber systems are complicated and that much remains to be done before the picture is clarified. The meaning of the ζ is obscure, and its significance, if any, in the colloid chemistry of papermaking stocks is not yet proved. As has been shown, the main difficulty arises from the complex nature of the fiber/liquid interface, and yet it is this interface which is of considerable importance in papermaking. Very little is known of the chemistry of the exposed surfaces of swollen fibers. Most studies of swollen polymers deal with the bulk properties of the material since it is bulk swelling that is generally of primary interest. Although the paper chemist is likewise interested in the bulk properties of swollen fibers, he has a particular interest in the fiber surface since this is the seat of interfiber bonding.

One of the most useful tools in studying the fine structure of fiber surfaces is the electron microscope whose limit of resolution is better than 100 A. Unfortunately, its use has thus far been restricted to dry shrunken surfaces whose structure only remotely resembles that in the swollen condition. The electrokinetic phenomena have their origin in the double layer whose magnitude, coincidentally, is of the same order as the limit of resolution of the electron microscope. It is conceivable that, with further development of theory and technique, electrokinetic studies can cast some useful light upon the structure of the swollen surfaces of fibers and serve as a supplementary source of information. In the meantime, caution should be exercised in attributing fiber properties and certain modes of fiber behavior to the classical concept of the zeta-potential.

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Fiber Surface Effects in Their Relation to Papermaking

HARRY F. LEWIS

The purpose of this paper is to relate the current knowledge of the arrangement of cellulose and the isotropic material in the primary and secondary walls of the fiber to the papermaking process, as these are determined by the electron microscope and cinephotographs. It is rather certain, from the result of the evidence, that the cambial wall is a network of fibrils, and that the secondary wall has parallel bundles of fibers of the same general dimensions. Beating removes two materials, namely, whatever the primary wall may be on the fiber and a portion of the outer zone of the secondary wall to permit extensive swelling of the middle zone of the secondary wall. The ordinary course of beating involves only the beginning of this process. Beating for glassine carries the process more nearly to completion. Degradation of the fiber by oxidation or acid hydrolysis greatly lowers the stability of the materials making up these two areas of the fiber structure to the point where the fiber falls apart under mechanical treatment. The presence of mannan in the limiting wall of the fiber is described. Whether this mannan fraction is responsible for the haze in solutions of cellulose acetate from wood pulps is not known but is strongly indicated.

In the papers presented in the first session, reference was made to the fine structure of the cellulose fiber. The purpose of the present paper is to relate our current knowledge of the arrangement of cellulose and the isotropic material in the primary and secondary walls of the fiber to the papermaking process, as these are determined by the electron microscope and the cinephotomicrographs.

Time will not permit a historical treatment of the developments behind the concepts of fiber structure presented by Kerr and I. W. Bailey (*6*), Frey-Wyssling (*5*), and others. Advantage will be taken of a very adequate review by S. H. Clarke (*4*) on the subject "Fine Structure of the Plant Cell Wall" to provide the starting point.

Clarke has presented a diagrammatic representation of cell-wall structure which is reproduced in Fig. 1. This shows the arrangement of the cellulose chain molecules, a group of microfibrils, the cellulosic and noncellulosic systems in the secondary wall, the cellulosic and noncellulosic systems in the primary wall, and a sketch showing the relative sizes and arrangement of the cell-wall constituents as revealed by microscopic examination.

Of particular interest to us are the representations of the primary and secondary fiber wall structure. According to Frey-Wyssling, the primary wall is made up of slender cellulose strands in an irregular arrangement with intermicellar zones occupying a large proportion of the whole wall, a representation which is supported by the fact that the primary wall is much more heavily lignified than the secondary wall. The primary wall is anisotropic in cross section but not as strongly so as is the secondary wall. This wall is made up principally of cellulose with large proportions of hemicellulosic and pectic materials together with lignin. Beneath the primary wall is the thicker secondary wall which is made up of a number of lamella and, in the natural state in wood, appears to be zonated into an outer zone, a middle zone, and an inner zone. The outer zone is made up of cellulose fibrils or strands arranged in approximately a flat spiral; this zone appears to be more heavily liquefied than is the remainder of the secondary wall. The middle zone of the secondary wall, which represents the principal portion of the layer, consists of cellulose strands arranged in concentric layers or sleeves almost parallel to the fiber axis or in counterclockwise helixes of steep slope. In an earlier paper, Clark pointed out how these slopes may be determined and directed our thinking toward the possibility that their orientation may play a significant role in the papermaking properties of our pulpwood. In some fibers there is an inner zone to the secondary wall in which, again, the cellulose fibrils are arranged in approximately a flat spiral.

SWELLING STUDIES

The experimental material in the first part of this paper will deal with the application of the cinephotomicrographic techniques to the general subject of the relation between the previous treatment of a fiber and its behavior on swelling. Carpenter and Lewis (*3*) pointed out in 1934 that, to a certain degree, the treatment received by a pulp fiber controlled its swelling behavior and that there was a general relationship existing between the type of swelling behavior with cuprammonium solution and pulp strength. Very raw, highly lignified fibers, on treatment with cuprammonium, behave as though they were encased in a nonyielding insoluble skin in which, because of differential delignification, small local zones of swelling could be observed. Carefully pulped and strong unbleached and bleached sulphite fibers, on treatment with cuprammonium solution, give the characteristic beading. Fibers degraded by heat, acids, or oxidation no longer were covered with a tough unyielding insoluble skin; instead, the skin was now in a condition whereby it dissolved readily in the swelling agent and units similar to Ritter's fusiform bodies (*17*) appear; these in turn break down into smaller and shorter units. Lewis and Richardson (*7*) studied the swelling behavior of kraft pulps in various stages of delignification. Pulps having 22.2 and 17.7% of lignin, respectively, were swollen only to a very slight degree by cuprammonium, and in no case could ballooning be observed. These pulp fibers appeared to be covered with a sheath of stiff, nonswelling, and nonelastic lignin. Pulps having 15.9 and 12.7% lignin showed some swelling and incipient bal-

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looning. The pulp having the lowest lignin content (8.6%) showed considerable ballooning and solution of the fiber in the swelling agent. In the latter case the outer lignin sheath had almost entirely disappeared and what lignin remained was largely in the wall of the fiber. Harlow (*5a*) confirmed these observations; in his work,

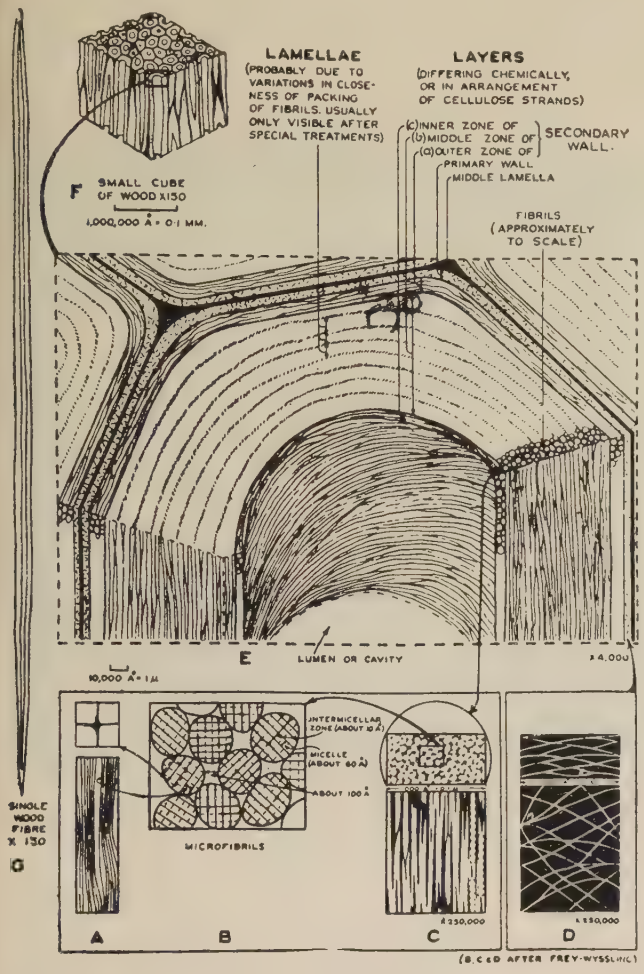

Fig. 1. Diagrammatic representations of cell-wall structure

A. Cellulose chain molecules, showing here and there zones of regular and parallel arrangement (the micelles indicated by x rays); *B*. group of microfibrils, showing approximate relative sizes of micelles and spaces revealed by study of material impregnated with silver; *C*. cellulosic and noncellulosic systems in the secondary wall. Cellulose white, noncellulosic materials black; transverse section above, longitudinal section below. Large circle indicates approximate size of fibril at same magnification. (Note that the dimensions given by the author of Figs. B and C do not correspond exactly, but they serve to indicate the approximate sizes. The linking arrows have been inserted by the present writer.) *D*. cellulosic and noncellulosic systems in the primary wall. Cellulose white, noncellulosic materials black; transverse section above, longitudinal sections below; *E*. small piece of wood showing the relative sizes and dispositions of the cell-wall constituents as revealed by microscopic examination; *F*. small cube of wood fibers magnified 150 times; and *G*. single wood fiber magnified 150 times.

he carried the delignification down to 3.0%. The strongest pulp, containing 6.5% lignin, showed the most general and conspicuous ballooning.

In the work to be described (which was initiated by Miss Olga Smith in 1932 in the Institute laboratories and which has been continued since then by other investigators) a cinephotomicrographic technique developed by Miss Smith has been used. Selected illustrations have been taken from our film collection, and in some cases the original titles have been included for their historical value, although the actual explanation of the swelling behavior and its relation to pulp and papermaking has been modified in line with advancing knowledge.

We are purposely limiting our discussion to pulps which have been fairly well delignified—in fact, the majority of the experiments have been made with unbleached and bleached spruce Mitscherlich fibers. The lignin content of such pulp is low and the hemicellulose content is optimum for good papermaking.

When a well-bleached spruce Mitscherlich fiber is carefully swollen with dilute cuprammonium hydroxide solution on a microscope slide, the swelling agent penetrates the fiber in increasing amounts. This first causes a swelling of the secondary wall. The pressure thus developed finds relief at the weakest point in the fiber—this may be at the fiber tip which gives way with subsequent rather violent emergence of the solution under pressure in the localized area being relieved—or it may be that the pressure is built up further down the fiber to such a degree as to rupture the nonelastic outer wall in a plane parallel to the orientation of the crystallites in this

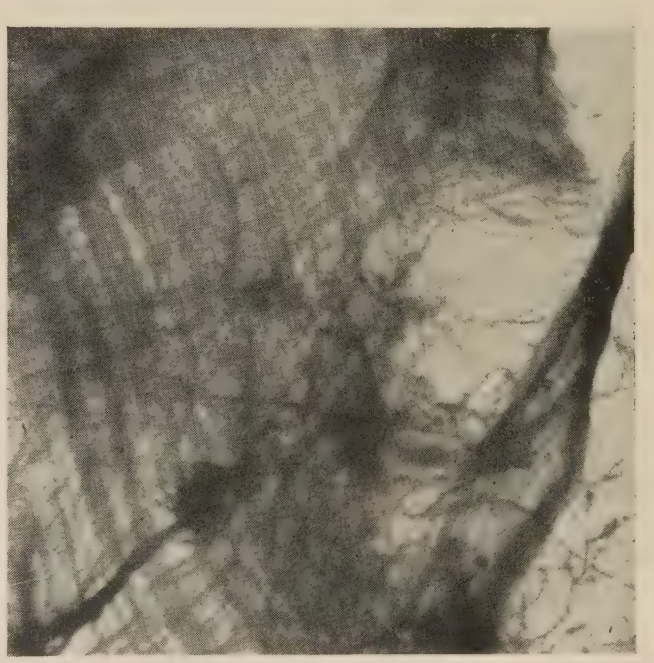

Fig. 2. Unbleached sulphite spruce pulp, beaten 20 min. X 4400

wall. The swollen secondary wall pushes out through the rupture, and gradually distends the crack until it completely encircles the circumference of the fiber, thus forming the characteristic balloon. As the balloon forms, the outer wall is rolled back on either side of the rupture and the connecting thread or thin ribbon of primary wall will be seen on the surface of the balloon. A whole series of balloons soon appear to give the impression of a string of beads. According to Bixler (*1*), it is the cambial wall which is thus rolled back. However,

the evidence would seem to favor the idea it is the laterally oriented outer zone of the secondary wall that is thus rolled back; the primary wall may be associated with it.

A good papermaking sulphite pulp has an outer wall strongly resistant to swelling and a central zone capable of a high degree of swelling in cuprammonium solution—the combination is able to form balloons of considerable relative size. The first swelling pictures will illustrate this characteristic behavior. A second sequence was taken with polarized light to show the orientation of the crystallites in the outer wall in the direction crosswise to the fiber axis and also the orientation of the fibers parallel to the fiber axis in the rings of primary wall bounding the balloon.

A variety of causative agents will bring about deterioration in fiber quality. Among these might be listed pulping for too long a time at too high a temperature, the use of too much bleach or bleaching in the range of pH 7, the presence of acids in contact with the fiber, and exposure of the fiber to high temperatures or to the harmful effect of light—particularly ultraviolet light. Any one or a number of these or other agents or conditions may be active in lowering the quality of commercial pulps.

Oxidizing agents and acids seem to affect particularly

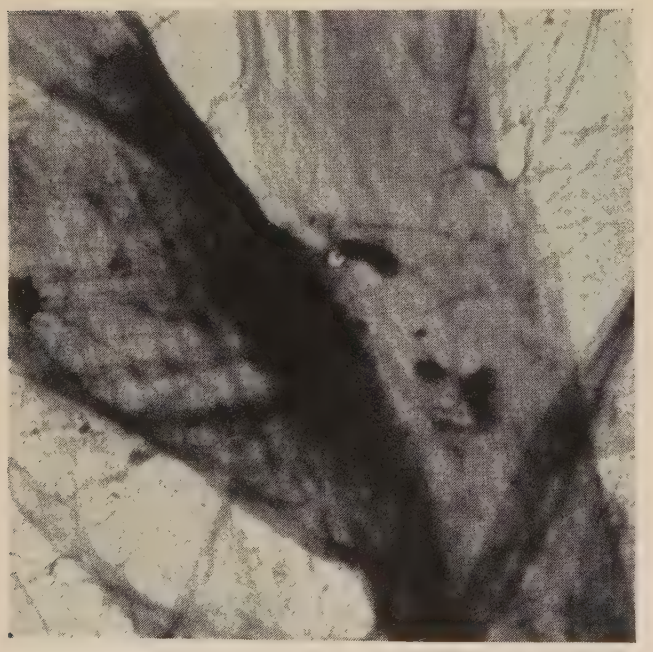

Fig. 3. Unbleached sulphite spruce pulp, beaten 42 min. X 4400

the stability of the outer wall and, in exaggerated cases, the outer wall can be seen dissolving in the cuprammonium solution as the swelling agent enters the secondary wall of the fiber. Ballooning, therefore, cannot occur and, indeed, before any noticeable swelling of the central zone of the secondary wall takes place, the fiber disappears by solution. Degradation by excess heat appears to be attended by transverse cracks occurring in the primary wall; the swelling agent enters the fiber through these cracks and rapidly dissolves the fiber contents without any extensive preliminary swelling.

The second set of swelling pictures illustrates this lowered resistance of the fiber wall to swelling agents and the ease with which the fiber is disintegrated by these same agents. Something of this same kind will occur during the beating of these degraded pulps; the result is a fiber mush with little fibrillation; poor quality is bound to result.

One very interesting sequence in this series shows the swelling behavior of a basswood fiber isolated by macera-

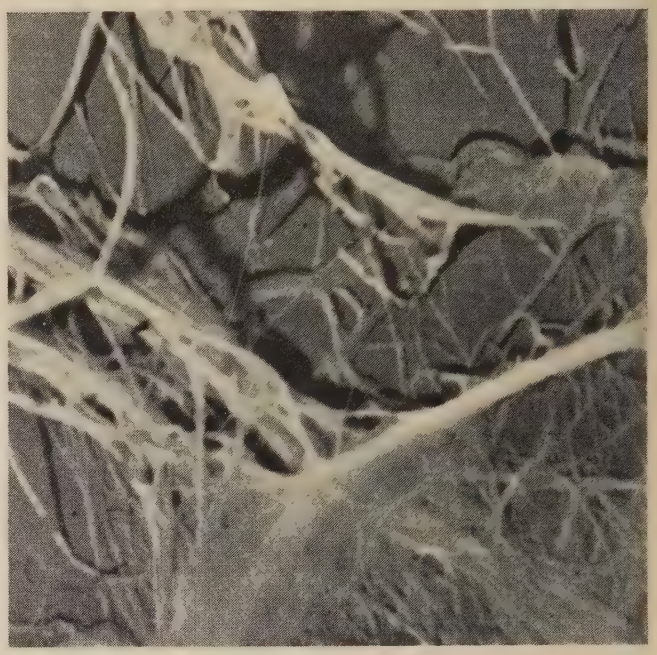

Fig. 4. Unbleached sulphite spruce pulp, beaten 42 min.; chromium shadowed at 45°; calculated thickness, 45 A. X 19,600

tion with potassium chlorate and nitric acid. This is the condition followed by Ritter in his classical work described at the last Fundamental Research Symposium in Madison (*17*). In this case, both oxidation and hydrolysis are carried to an extreme degree, and it is possible to see the primary wall dissolving in the cuprammonium solution. Immediately following the solution of the primary wall, the structure of the secondary wall appears to break up into the structures described by Ritter as fibrils and fusiform bodies—as though the solvent had dissolved first what might be considered the more readily accessible and reactive forms of the cellulose, leaving the bundles of crystalline cellulose to pass into the solvent stream; these break up into smaller units which, in turn, quickly go into solution. In this picture, one undissolved remnant of the primary wall remains, and the secondary wall particles which are caught in this constriction are the last to go into solution. This is somewhat akin to the statement of Frey-Wyssling (*5*) that "maceration consists, on the one hand, of separating the microfibrils longitudinally and by physical-chemical forces and, on the other, of hydrolyzing them transversely. Hydrolysis proceeds along predetermined planes of the chain lattice."

One swelling sequence has been included to demonstrate that it is also possible to purify a pulp to the point

of no return as far as papermaking goes. This pulp, which was supplied to us some years back by Fred Olson of the Cellulose Research Corp., had an alpha-cellulose content of 99.1% and a pentosan content of 0.70%. After 90 minutes of careful beating, the freeness showed no drop nor was there any indication of hydration; in fact, the sheets were so weak they could not be handled in spite of the high pulp purity and a TAPPI viscosity of 32 cp. Swelling studies showed the apparent removal of the noncellulosic material present

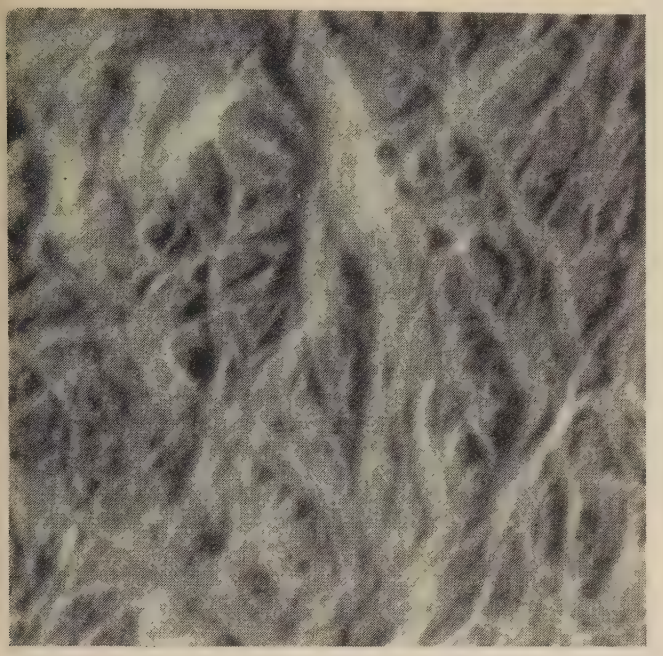

Fig. 5. Unbleached sulphite spruce pulp, beaten 42 min.; gold shadowed at 45°; calculated thickness, 17 A. X 44,000

between the various layers in the secondary wall of the fiber and of the lignin and hemicelluloses in the outer zone of the secondary wall, immediately below the primary wall. As a result, in a portion of the film at least, the swelling agent, before it was able to build up a solution pressure within the secondary wall of sufficient dimension to rupture the primary wall, caused the endwise telescoping of one layer from the next until the entire secondary wall has disappeared. There is also evidence to show that at least a part of the primary wall has been removed to a considerable degree in the process of purification.

The final sequence of cinemicrographs shows rather clearly what happens as beating proceeds. The early stages of beating would seem to cause an unwinding of the transversely wound outer zone of the secondary wall and it really appears to be just that, with actual removal of increasing amounts of the wall. Where the wall has been removed, the central zone of the secondary wall is exposed and this swells as hydration proceeds. With continued beating, more and more of the outer wall is removed and, in the swelling pictures with cuprammonium hydroxide, the secondary wall, no longer limited in its extensibility by the rigid outer wall, swells to a diameter two to three times that of the original fiber. The cinemicrographs show residues of the outer zone of the secondary wall which exert their usual constricting influence on the extension of the secondary wall. It is possible to carry the beating operation to the point where all the outer wall is removed. This would seem to be the ideal point for glassine manufacture were it not for the fact that beating is essentially a heterogeneous phenomena in which some fiber are overbeaten, whereas others are underbeaten and the happy medium for the particular quality of paper desired is merely the result of balancing one condition against its opposite; however, it would seem to be theoretically possible to achieve a beating operation where extremes would be brought closer together and more satisfactory papers would result.

The condition of the fiber surface is thus seen to play some part in determining the quality of paper which may be made from a given pulp, although it is only one of the various factors which enters into the over-all operation.

As an addendum to the discussion on the swelling behavior of fibers, attention should be called to the fact that there seems to be a membrane which may be associated with the outer zone of the secondary wall and which does not appear to dissolve in the cuprammonium solution. This may be the true cambial wall. Dark field pictures of carefully swollen pulp fibers show the

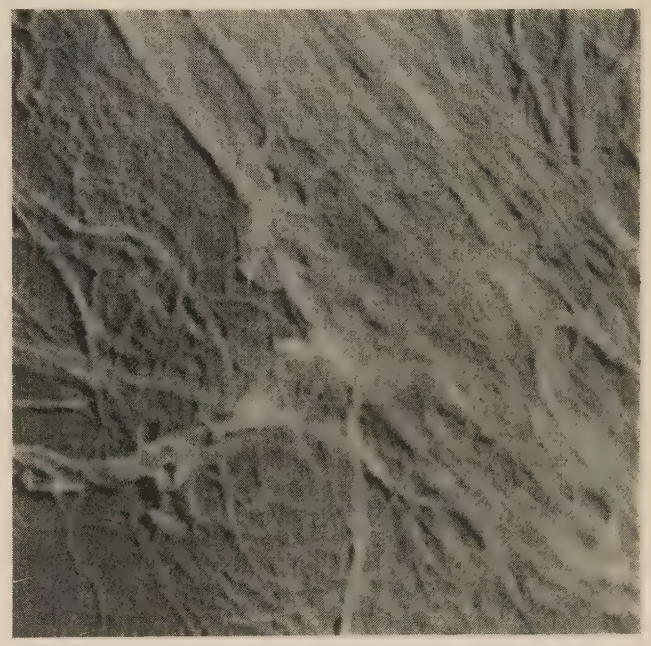

Fig. 6. Bleached aspen sulphite pulp, beaten 20 min.; chromium shadowed at 45°; calculated thickness, 60 A. X 19,600

presence of skinlike material having the shape of the swollen fiber after deflation. This material formed the basis for a study financed by TAPPI at The Institute of Paper Chemistry in 1937 (*2*). From a spruce Mitscherlich pulp having 85.3% alpha-cellulose, and 3.8% pentosan, and a viscosity of 40 cp., there was recovered from a cuprammonium solution of the pulp about 0.5 to 0.75% of a carbohydrate material which, on analysis, was shown to contain 44.2% carbon and 6.25% hydrogen (ash-free basis). For cellulose or other polyhexoses,

the calculated values are 44.44% carbon and 6.17% hydrogen. The product, on hydrolysis, gave better than 97% reducing sugar. Some 45% of the material appeared to be fermentable by yeast. The product was shown to be free of pentosans, uronic acid, and the methoxyl radical. Tests for galactose and mannose in the acid-hydrolyzed material were negative. The product, on acetylation, yielded an insoluble, horny acetate.

More recently Wise and his associates (*10*) had occasion to apply paper chromatography to this product after acid hydrolysis. To their surprise, the chromatograms indicated much more mannose than glucose. On analysis of the hydrolysate, 78% (ash-free basis) of the reducing sugar was found to be mannose. The cuprammonium-insoluble material, identified as the so-called skin substance by dark-field microscopy, seems to be a polysaccharide or a mixture of polysaccharides containing both glucose and mannose units, with the latter predominating. Since the acetylated product is insoluble in cellulose acetate solvents, it is suggested that cellulose acetate haze may be associated with this material and pulps for acetylation might receive some type of a treatment to remove the mannan. The highly purified pulp prepared by the Cellulose Research Corp. was found to be almost entirely soluble in cuprammonium solution.

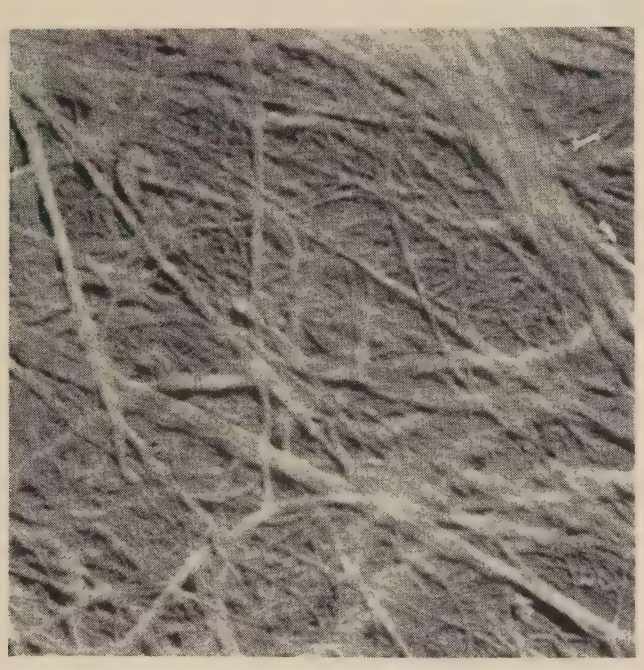

Fig. 7. Bleached aspen sulphite pulp, beaten 40 min.; chromium shadowed at 45°; calculated thickness, 60 A. X 19,600

This is in line with its swelling behavior. The pulp should yield an acetylated product free from haze.

No comprehensive study has been made to relate the insoluble residue with pulp properties but such a study would appear to be warranted. A doctorate thesis just being started in our laboratories will initiate fundamental work on the source and nature of mannose units in pulp fibers. Possibly in this work, time will permit a few experiments in the direction of clarifying the above indications.

ELECTRON MICROSCOPE STUDIES

The other part of this report deals with the nature of the fiber surface as indicated by electron microscopy. A good review of the subject was given by Siegel at the Madison Fundamental Research Conference in 1948. Wyckoff has presented a considerable amount of information in his recent book. Among the publications in this new field of particular interest, to this group might be listed those of Hock (*11*), Kinsinger and Hock (*12*), Williams and Wyckoff (*13*), Mühlethaler (*8*), Kuehn

Fig. 8. Cleaned cellulose fibrils forming the primary wall of pinewood. Collodion substrate. Chromium shadowing. X 13,500

(*14*), Sears and Kregel (*15*), and Husemann and Carnap (*16*). More recently, Hock (*18*) and Rånby and Ribi (*19*) have published interesting papers relating particularly to the electron microscope investigation of hydrolyzed cellulose.

One important conclusion which can be drawn from the electron microscopical studies of natural cellulose fibers is that they have a fibrillar structure—as Kinsinger and Hock put it: "They are composed of fine filaments of cellulose called fibrils." The dimensions observed vary with the source of the fibers and their treatment. In general, they appear to run from about 200 A. in diameter down to 60 A. Kinsinger and Hock report a lengthwise periodicity of approximately 150 A. Sisson (*9*) describes fibrils prepared from cotton wood pulp and rayon which had been prepared by treatment with an ultraresonator. These fibrils were long and slender and of varying diameter. The particular products from wood pulp had a maximum length of 3300 A. and a minimum length of 1200 A., or an average length of 1450 A.; the average chain length from measurements of the degree of polymerization was calculated as 1510 A. The thickness of these fibrils was 37 A. and the width was 45 A.—incidentally, these last values fall close to the limiting resolution of the electron microscope.

It should be pointed out that these dimensions, with the exception of those of Sisson, and the more recent electron micrographs of hydrolyzed cellulose (*18, 19*), do not check too well with dimensions of submicroscopic

structures determined by other methods. By x ray diffraction the micelle is found to be about 50 A. in diameter and 500 A. long. From the degree of polymerization of hydrolyzed cellulose, the more highly ordered regions in cotton consist of 280 glucose units with a length of approximately 1450 A.

Some recent photographs taken with the electron microscope at the Institute are shown in Figs. 2–7. which show hardwood and softwood pulp fibers at different stages of beating.

Fig. 9. Cellulose from cleaned secondary wall of pinewood. Collodion substrate. Chromium shadowing. X 18,000

The second indication of interest has to do with further evidence for the nature of the structural difference between the primary or cambial wall in a wood fiber and the secondary wall. As was mentioned in the first section of this paper, the primary wall is laid down while the plant cell is still growing—in contrast to the secondary wall in which cellulose continues to be deposited after longitudinal growth has stopped. Frey-Wyssling (*5*) has suggested an irregular arrangement of cellulose fibrils or strands as a result of growth of the wall by intussusception or the interposition of new molecules between the original material; in the primary wall (Fig. 8) the intermicellar zones occupy a larger proportion of the whole in line with the fact that the primary wall is more heavily lignified than is the secondary wall. This irregular arrangement is supported by the electron microscope. Mühlethaler (*8*) showed by chromium shadowing of cleaned cellulose fibrils in the primary wall of pure wood a criss-cross network of fibrils running in different directions; a similar picture of the secondary wall (Fig. 9) shows without question parallelism in the secondary wall. The outer wall of a carefully cooked and bleached pulp fiber would therefore appear to be made up of the criss-cross network of cellulose fibrils, possibly with some isotropic hemicelluloses and possibly lignin in the interfibrillar spaces (Fig. 10). Immediately beneath this would be the outer zone of the secondary wall in which the fibrils are arranged almost perpendicularly to the direction of the fiber axis. Beneath this is the middle zone of the secondary wall with its fibrils running more nearly parallel to the fiber axis. The secondary wall would be strongly anisotropic—the primary wall would be only weakly anisotropic, since the anisotropic cellulose in the fibrils would be masked by isotropic interfibrillar material and neutralized by the random orientation of the fibrils. Finally, there is the inner zone of the secondary wall—present in some fibers—in which the fibers are again arranged in a flat spiral.

To sum up this discussion, we have tried to show something of the relation between the surface of the fiber and its papermaking properties as these are indicated by cinemicrographs and electron micrographs. No attempt has been made to review the general literature.

The nature of the fiber surface is dependent upon the pulping reactions employed. As an exaggerated example of this, a pulp is described having a lignin content of 22.2%. The fiber surface in this case is intercellular material which has been shown by A. J. Bailey to be largely lignin. Pulp strengths, as measured by bursting strength and fold, are low relatively and the sheet qualities as shown by apparent density, stiffness, and porosity are poor. Such a pulp shows only slight swelling with cuprammonium solution and no ballooning. As the pulp is progressively delignified the strength and other sheet properties improve. When the lignin content has been reduced to 8.6%, the burst has improved by 47% and the fold by 1900%, the pulp hydrates more rapidly, and the apparent density of handsheets has increased from 8.7 to 12.0 at the same freeness. The latter pulp shows general ballooning when the pulp fibers are reacted with cuprammonium hydroxide, and only traces of intercellular material are visible on the walls of the balloons.

Fig. 10. A sheet of lignin remaining after the acidic saccharification of the cellulose. Collodion substrate. Chromium shadowing. X 15,000

As the intercellular material is removed by delignification during pulping or bleaching, any material not dissolved will become a part of the new surface

in this case the primary or cambial wall made up of a criss-cross network of cellulose fibrillar bundles in which the cellulose is anisotropic and in which are interdeposited those interfibrillar constituents which are not dissolved by the delignification operations. Immediately beneath this is the outer zone of the secondary wall of the fiber with its fibrils wound in a transverse direction tightly around the fiber.

As beating progresses, this surface material is brushed from the fiber, thus exposing the outer layer of the secondary wall and this, in turn, is brushed off to lay bare the middle zone of the secondary wall which hydrates and swells very greatly, provided the cellulose has not been greatly degraded. These swollen secondary walls, made up of distended cellulose fibrils, form a bond which, on drying, gives a sheet of the type of glassine. Where the beating has progressed only a part of the way, the fibrillar material from adjoining fibers forms a bond with the exposed and highly hydrated areas of the secondary wall.

When fibers are degraded by oxidation or by hydrolysis, the cellulose (and other components) are rendered more soluble by shortening of the molecular chain length and by the introduction of carboxyl groups, and these tend to be removed readily in beating or with swelling agents before the secondary wall has developed its gel structure (Fig. 11) and, as a result, the fiber is disintegrated in the beater or in the presence of cuprammonium solution.

Fig. 11. Cellulose fibrils being split into short fragments under the action of hydrogen peroxide. Collodion substrate. Chromium shadowing. X 11,000

We have presented a picture of the role of the fiber surface in the papermaking process. Not all of the picture can be demonstrated by established results, but we can be rather certain, from the result of electron microscopic evidence, that the cambial wall is a network of fibrils, that the secondary wall has a parallelism, and that these fibrils may be around 35 to 100 A. in diameter; this last is only conjective since 50 A. is the limiting resolution of the electron microscope. They may go all the way to individual chain molecules. We can also be fairly certain from the same source that the secondary wall has parallel bundles of fibrils of the same general dimensions.

We are also rather certain, as shown by the cinemicrographs, that beating results in a removal of two materials—namely, whatever primary wall may be on the fiber and a portion of the outer zone of the secondary wall, the quantity removed depending on the time and severity of beating—to permit extensive swelling of the middle zone of the secondary wall. The ordinary course of beating involves only the beginning of this process. Beating for glassine carries the process more nearly to completion. Finally, we are certain that degradation of the fiber by oxidation or acid hydrolysis (such as excess cooking) greatly lowers the stability of the materials making up these two areas of the fiber structure to the point where the fiber falls apart under mechanical treatment.

The presence of mannan in the limiting wall of a fiber has been described. Whether this is laid down in the cambial wall by intussusception is not known—nor is it certain whether it is in the cambial wall or in the outer zone of the secondary wall. Whether this mannan fraction is responsible for the haze in solutions of cellulose acetate from wood pulps is not known but is strongly indicated. A study of the nature of the mannose-containing materials is now being initiated at the Institute.

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Figures 8, 9, 10, and 11 are from R. W. G. Wyckoff "Electron Microscopy" Copyright, 1949, Interscience Publishers, Inc.

Fifth Engineering Conference

The Fifth Engineering Conference of the Pulp and Paper Industry, sponsored by the TAPPI Engineering Division will meet at the Netherland Plaza Hotel, Cincinnati, Ohio, on Oct. 2–5, 1950. George H. Pringle, Asst. Chief Engineer of the Mead Corp., Chillicothe, Ohio, will be General Chairman. The tentative program follows:

Meeting of Monday, October 2

8:30 a.m. REGISTRATION (*Fourth Floor Foyer*)

9:00 a.m. Opening Remarks by the *General Chairman* and A. E. Bachmann, *President* TAPPI

9:30–
11:00 a.m. MILL DESIGN AND ECONOMIC ASPECTS SESSION
Alvin H. Johnson, Consulting Engineer, New York, N. Y., Chairman
"Paper Machine Drives," by Roland A. Packard, Holyoke Machine Co., Holyoke, Mass.
"Engineering Planning for Handling Mill Waste Waters," by H. W. Gehm, National Council for Stream Improvement, New York, N. Y.

11:00–
12:30 p.m. HYDRAULICS SESSION
K. J. Mackenzie, Eastman Kodak Co., Rochester, N. Y., Chairman
"Progress Report on Flow of Paper Stock in Pipes Project," by Mr. Mackenzie

12:30–
2:00 p.m. LUNCHEON (WHERE YOU WILL)
(Rooms have been reserved for luncheons for each committee in the Engineering Division)

2:15–
3:45 p.m. ENGINEERING RESEARCH AND MACHINE DESIGN SESSION
John D. Lyall, Armstrong Cork Co., Lancaster, Pa., Chairman
1. "The Application of Enclosed Gearing in the Pulp and Paper Industry," by F. Richardz, Westinghouse Electric Corp., Pittsburgh, Pa.
2. "Air Removal from Stock Ahead of the Head Box," by C. L. Clark and J. A. Smith, Clark & Vicario Co., Bronxville, N. Y.

3:45–
5:15 p.m. MATERIALS HANDLING SESSION
A. P. Schnyder, Ebasco Services, Inc., New York, N. Y., Chairman
"Outstanding Practices in Materials Handling in the Pulp and Paper Industry on the West Coast," by F. D. Helverson, Crown Zellerbach Corp., Portland, Ore.
"Handling of Finished Pulp and Paper Products from the Machine to the Shipping Dock," by H. F. R. Weber, Link-Belt Co., Chicago, Ill.

Meeting of Tuesday, October 3

8:45–
10:30 a.m. MILL MAINTENANCE AND MATERIALS SESSION
H. F. Parker, New York and Pennsylvania Co., Lock Haven, Pa., Chairman
1. "Teflon in Process Equipment," by D. B. Hanson, E. I. duPont de Nemours & Co., Inc., Wilmington, Del.
2. "Slotted Screen Plates for Pulp and Paper Mills," by Henry W. Downs, Jr., Union Screen Plate Co. of Canada, Ltd., Lennoxville, P. Q.

10:30–
11:00 a.m. DATA SHEETS SESSION
Henry J. Perry, Paper Trade Journal, New York, N. Y., Chairman
"Progress Report," by Mr. Perry

11:00–
12:30 p.m. DRYING AND VENTILATING SESSION
M. L. Barker, Beckett Paper Co., Hamilton, Ohio, Chairman
"Drying 800-tons Kraft Paper Daily on One Machine," by L. C. Crowder, Macon Kraft Co., Macon, Ga.
"The Ross Pulp Drier" by J. F. Schwind, J. O. Ross Engineering Corp., New York, N. Y.

12:30–
2:00 p.m. LUNCHEON (WHERE YOU WILL)

2:00 -
3:30 p.m. MILL MAINTENANCE ROUND TABLE
"Maintenance of Mill Roofs," by G. F. Hrubecky, Marathon Corp., Menasha, Wis.

2:00–
3:30 p.m. MATERIALS HANDLING ROUND TABLE
Discussion of Materials Handling Problems

2:00–
3:30 p.m. DATA SHEETS ROUND TABLE

3:30–
5:00 p.m. DRYING AND VENTILATING ROUND TABLE
Discussion of Drying Problems

3:30–
5:00 p.m. ENGINEERING RESEARCH AND MACHINE DESIGN ROUND TABLE
"Thoughts on Standardization," by G. E. Clink, Sandy Hill Iron & Brass Works, Hudson Falls, N. Y.

7:00 p.m. DINNER (Sponsored by the Allied Industries in the Cincinnati Area)

Meeting of Wednesday, October 4

8:45–
10:30 a.m. STEAM AND POWER SESSION
C. J. Sibler, West Virginia Pulp and Paper Co., New York, N. Y., Chairman
"Installation and Operation of the 1200-lb. Steam Plant at the Union Bag & Paper Corp.. Mill," by H. R. Arnold, Union Bag & Paper Corp., Savannah, Ga.
"The Dual Circulation Boiler," by H. B. Wallace, Jr., Foster-Wheeler Corp., New York, N. Y.

10:30–
11:00 a.m. CHEMICAL ENGINEERING SESSION
James R. Lientz, Union Bag & Paper Corp., Savannah, Ga., Chairman
"Progress Report of the Digester Corrosion Committee," by Mr. Lientz

11:00–
12:30 p.m. ELECTRICAL ENGINEERING SESSION
Albert S. Goodrich, Hammermill Paper Co., Erie, Pa., Chairman
"The Selection of Electric Motors for Paper Mill Application," by R. F. Sorenson, Union Bag & Paper Corp., Savannah, Ga.

12:30–

2:30 p.m. Engineering Division Luncheon

2:30–
5:00 p.m. Steam and Power Round Table
"Purchases vs. Generated Power Costs"
"Emergency Shut-Down of Recovery Boilers"

2:30–
5:00 p.m. Mill Design and Engineering Aspects Round Table
Discussion of Mr. Packard's Paper

2:30–
5:00 p.m. Electrical Engineering Round Table
"Couch Power Requirements"

2:30
5:00 p.m. Chemical Engineering Round Table
Discussion of Digester Corrosion

Program for Thursday, October 5

Plant Visits

1. Cincinnati Trip: Allis-Chalmers Mfg. Co., Cincinnati Rubber Co., and Cincinnati Milling Machine Co.
2. Hamilton Trip: Black-Clawson Co., Economy Pump Co., and Shuler & Benninghofen Co.
3. Luncheon at Middletown, Ohio
4. Choice of trips to: American Rolling Mill, Shartle Bros. Machine Co., and the new Hutchins Power Station near Miamisburg, Ohio

Special TAPPI Issue of Cenco News Chats

The 1950 Summer Issue, No. 68 of Cenco News Chats, published by the Central Scientific Co., 1700 Irving Park Road, Chicago 13, Ill., is partly devoted to the Technical Association of the Pulp and Paper Industry. A limited number of copies are available to those who request them.

On the front cover is a large and accurate sketch of William G. MacNaughton (1874–1949), former Secretary-Treasurer of TAPPI. A biography of Mr. MacNaughton is published in the issue. A print of this sketch will be sent to anyone who requests one.

The write-up of the Technical Association features a two-color presentation showing the TAPPI seal and the distinctive front cover of *Tappi*. There is a brief review of the association services, the divisional and sectional structure, a list of the TAPPI Medallists and the administration. The circulation of Cenco News Chats is 65,000.

Changes in Assignments of TAPPI Methods

In the Report of the Standards Committee for 1949, published in *Tappi* 33, No. 3: 88A (March, 1950), there was included an appendix giving the jurisdiction of the various committees over TAPPI Standards and Methods. The following changes have since been authorized.

Committee	Add	Subtract
Chemical Methods	T 11 m	T 451 m
Container Testing	T 472 m	...
Fibrous Materials Testing	...	T 11 m
Microscopy	T 445 m	T 631 m, T 534 m
Optical Properties	T 218 m	...
Packaging Materials Testing	T 448 m, T 436 m, T 464 m, T 465 m	T 472 m
Paper Testing	T 451 m	T 445 m, T 448 m, T 463 m, T 464 m, T 465 m
Pulp Testing	...	T 218 m
Wax Testing	T 630 m, T 634 m	...

Tappi Copyright

The Technical Association of the Pulp and Paper Industry has been issued Trade Mark Certificate No. 527349 by John A. Marzall, Commissioner of Patents, as of July 4, 1950. This refers to the word *Tappi* as it appears on the front cover of this magazine. Application for this registration was prosecuted by Joseph Rossman, Counsellor in Patent and Trade Mark Causes, 1820 Jefferson Place, N. W., Washington 6, D. C. Mr. Rossman is a member of TAPPI.

Alkaline Pulping Conference

R. R. Fuller, Program Chairman of the TAPPI Alkaline Pulping Conference to be held at the George Washington Hotel, Jacksonville, Fla., on Oct. 25–27, 1950, has announced the following tentative program:

Meeting of Wednesday, October 25

Morning Session—9:30 a.m.

1. Review of Literature of Causticizing
2. Causticizing Sodium Carbonate Solutions
3. Effect of Sulphidity
4. Sodium-Sulphur Compounds
5. Operation of Causticizing Equipment
6. Sulphate Pulp Mill Design for Abatement of Odor and Effluent Nuisance, by W. O. Hisey, South African Pulp and Paper Industries Ltd., Johannesburg, S. A.

Afternoon Session—2:00 p.m.

1. Review of Literature on Rotary-Lime Kilns
2. Economics of Short Kilns vs. Long Kilns
3. Long-Kiln Operation
4. Short-Kiln Operation
5. Bird Centrifuge for Sludge Washing and Thickening
6. Panel Discussion on Kiln Operation

Meeting of Thursday, October 26

Morning Session—9:30 a.m.

1. Pressure Washing
2. Effect of Wood Storage on Yield and Quality
3. Wood Storage
4. Cooking at Constant Temperature and Constant Concentration
5. A New Type Condenser

Afternoon Session—2:00 p.m.

1. Wet-Strength Resins and Additives
2. Mill Effluents
3. Meeting of Alkaline Pulping Committee

Program for Friday, October 27

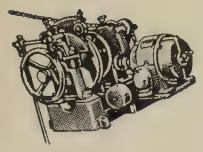
All-day tour of Northern Florida, including a visit to the Engineering Experiment Station of the University of Florida at Gainesville and the mill of the Hudson Pulp and Paper Company at Palatka.

Following the Palatka visit the Conference will be guests of the Noble & Wood Machine Co., at Welaka, Fla. Luncheon will be served at Gainesville and dinner at Welaka.

Henry Vranian of the Chesapeake Corp., West Point, Va., will be General Chairman of the Conference. E. A. Harper of the Hudson Pulp and Paper Co., is Chairman of the Arrangements Committee.

Fibrous Agricultural Residues Conference

A full-day conference is planned for Monday, November 13, on the production of strawboard for corrugating, with emphasis on processing and refining of the strawboard stock. Tuesday, November 14, will be devoted to a meeting of the Fibrous Agricultural Residues Committee of TAPPI and to plant visits in the Peoria area. If there will be time and the



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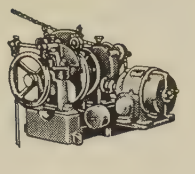

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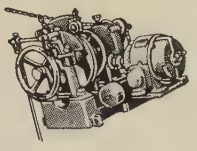

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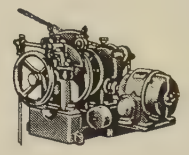

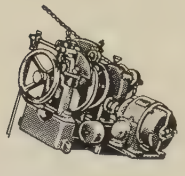

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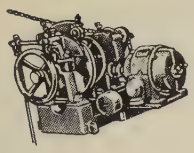
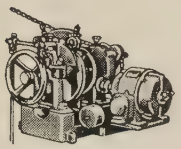
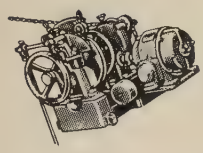




AFTER CENTRIFUGAL PUMPS

AHEAD OF BROWN STOCK WASHERS



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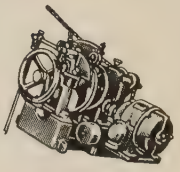

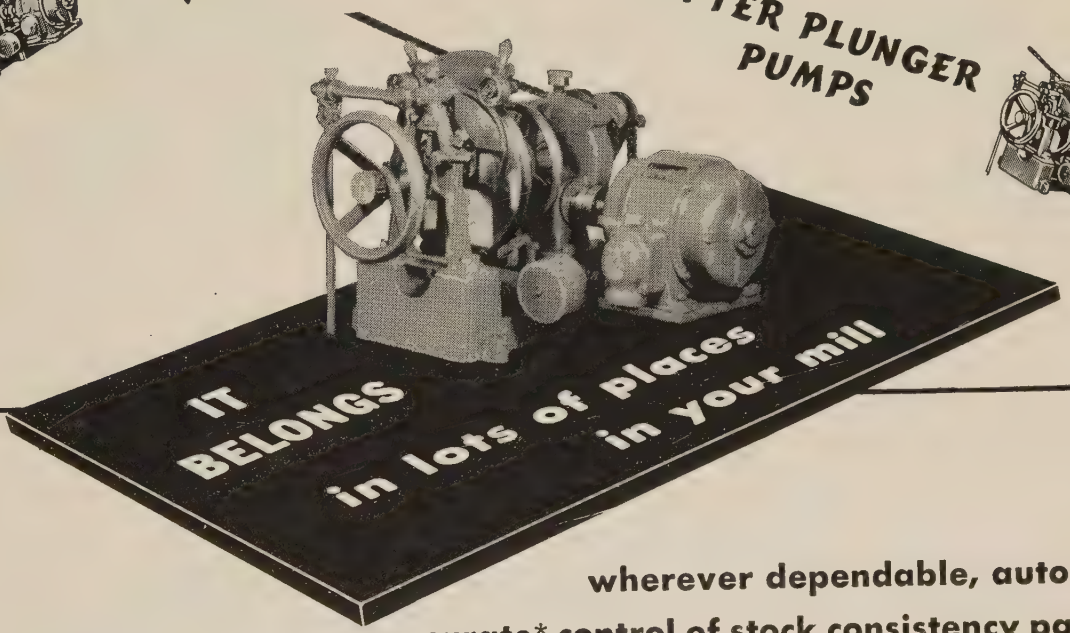

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group desires it, continued discussion of Monday's program can be held.

Papers for presentation at this meeting are being solicited from the strawboard mills and from equipment manufacturers on washing, screening, refining and other phases of strawboard production. These presentations will be relatively short, about 10 minutes, thus allowing sufficient time for full and detailed discussion of these phases of strawboard production. If you or anyone in your organization have some data or information which you think might be of interest to the technical men, operators, and executives of the strawboard industry who will be present at this meeting, please let me know immediately and I shall be glad to put you on the program.

A social hour and a group dinner will be held on Monday evening, November 13, at the beautiful new Blue Ribbon hall of the Pabst Brewing Company at Peoria Heights. A prominent speaker will be obtained to address the group at the dinner. A small registration fee will be charged to just cover the cost of the dinner and the incidental expenses of this meeting.

A large block of rooms has been reserved at the Pere Marquette Hotel in Peoria for the nights of November 12 and 13. Please make your reservations, now, directly with this hotel, stating this reservation is in connection with the TAPPI meeting.

Further notices will be sent you as soon as the detailed arrangements of the program have been made and the titles of the papers and names of authors are available.

Very interesting papers and discussions are expected at this meeting. Please plan to attend yourself and bring with you others of your organization who are interested in this work. The more people there are present at these meetings the better the discussions and the greater the benefits that are derived by all.

S. I. Aronovsky, *Chairman*
Fibrous Agricultural Residues Committee

Second Testing Conference

The Second Testing Conference of the Technical Association of the Pulp and Paper Industry will be held in the Recreation Building of the Eastman Kodak Co., 200 Ridge Road West, Rochester, N. Y. Housing facilities will be provided by the Seneca Hotel, Rochester, N. Y., on September 13–15, 1950. Reservations at the Seneca Hotel should be made immediately with Mr. Earl F. Campbell, Resident Manager to assure accommodations.

To reach the Recreation Building a No. 1 bus leaves going west on Main Street, one block from the Seneca Hotel. Get off at Lake and Ridge Road. The Recreation Building is located at 200 Ridge Road West near this junction. Instruction sheets will be available at the Seneca and a guide or poster will indicate the direction to the Recreation Bldg., at the Lake-Ridge Road junction. Taxicabs will also be available at the Seneca Hotel.

A feature of the meeting will be an unusual opportunity to take a guided tour through the paper mill, the coating mill, and the photographic film-manufacturing plant. This will be the first time that all of these facilities are opened to industrial visitors.

The conference itself will be held work-shop style with each committee of the Testing Division devoting its attention to current problems relating to tests in process of development. It is hoped that all of the members of the committees of the Testing Division will attend. Nonmembers of committees will be welcome and company managers are urged to send the technical men of their organizations who are responsible for the maintenance of product quality.

Following is the tentative program:

Meeting of Wednesday, September 13

Gymnasium, Recreation Building, Eastman Kodak Co., Rochester, N. Y.

9:00 a.m. General Session
James d'A. Clark, General Chairman, Testing Div., presiding
1. Welcome to Kodak Park, by G. T. Lane, Asst. Manager, Kodak Park Works
2. Introductory Address, by James d'A. Clark
3. Pulp Characteristics in Relation to Testing Methods, by Albert E. Bachmann, Missisquoi Corp., Sheldon Springs, Vt., *President,* TAPPI

12:45 p.m. Luncheon (Recreation Bldg. Cafeteria)

2:00 p.m. Wax Testing
A. M. Heald, Marathon Corp., Menasha, Wis., Chairman
(This will be a meeting of the TAPPI-ASTM Joint Committee on Petroleum Waxes. An extensive program is being arranged that will require the full 3 days of sessions.)
Although Dr. Heald has not yet announced his program it is expected that there will be discussions on the reports of the following subcommittees: (1) Strength Tests; (2) Flow Tests; (3) Stability Tests; (4) Sensory Tests; (5) Composition (Melting Point and Oil Content, Melting Point Distribution); (6) Blocking; (7) Sealing and Laminating; and (8) Scuff-Gloss

2:00 p.m. Optical Properties
A. H. Croup, Hammermill Paper Co., Erie, Pa., Chairman
1. Gloss of Paper (Final draft of the proposed tentative standard)
2. Report on the Results of the Use of the National Bureau of Standards Fading Papers for Calibrating Fadeometers and the Possibility of Recommending These for General Use in the Industry

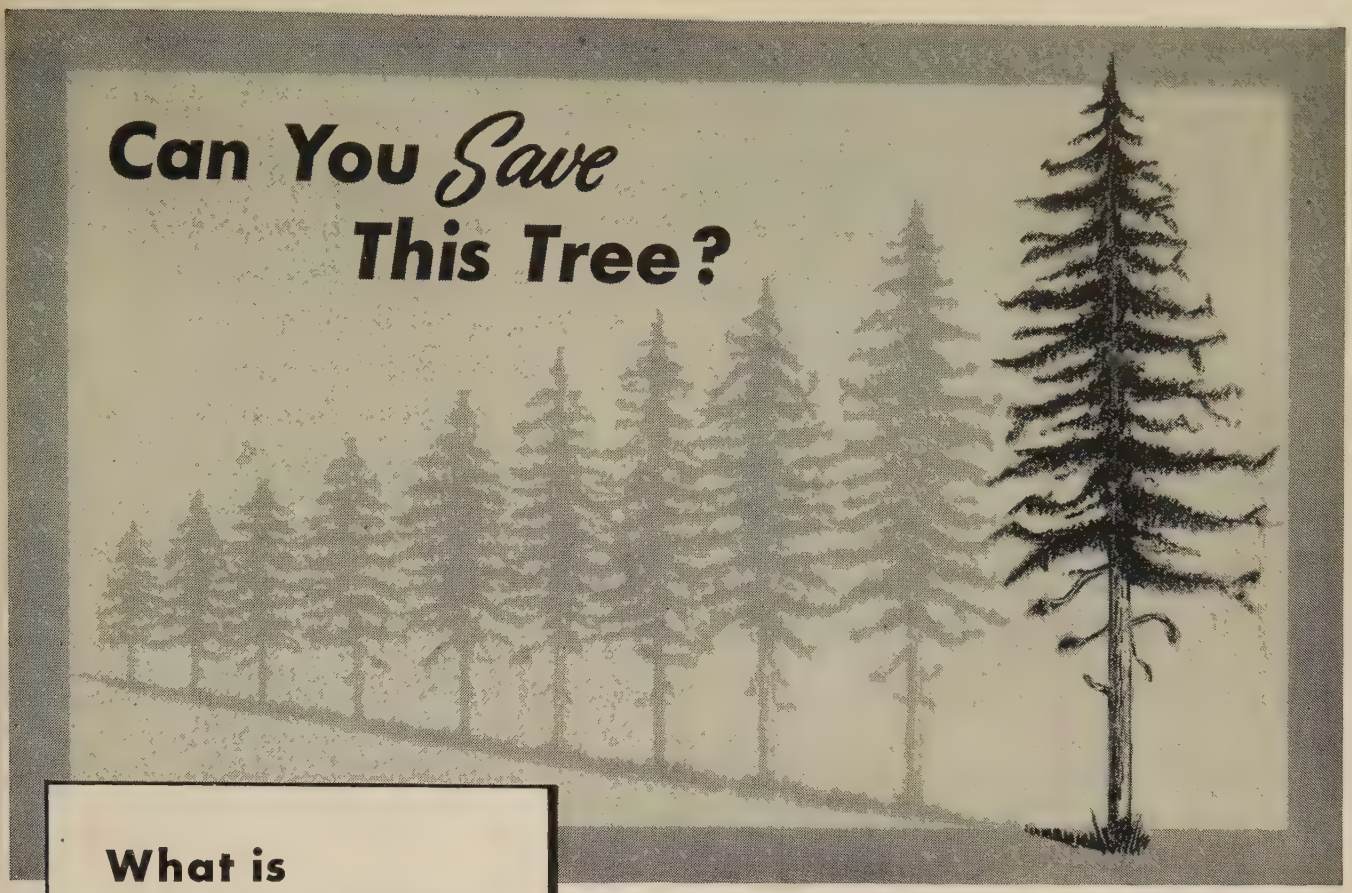
2:00 p.m. Nonfibrous Materials Testing
J. P. Casey, N. Y. State College of Forestry, Syracuse, N. Y., Chairman
(This Committee will hold two and possibly more sessions. The major consideration will be given to:
1. Testing of Starches
2. Analysis of Mineral Fillers
3. Analysis of Rosin Size
4. Testing of Clays

Other methods that will be given preliminary consideration are:
5. Analysis of Wax-Rosin Size
6. Testing of Sodium Aluminate
7. Testing of Foaming Agents

As time permits a number of the present TAPPI Standards will be reviewed.

2:00 p.m. Packaging Materials Testing
L. E. Simerl, Marathon Corp., Menasha, Wis., Chairman
(This Committee will require two or three sessions to cover its projected program.)
1. Water Vapor at Zero F. (Project 277)
2. Flavor and Odor Transfer (Project 328)
3. Testing Pressure-Sensitive Tapes (Project 330)
4. Water Vapor Permeability of Completed Packages (Project 357)

Can You *Save* This Tree?



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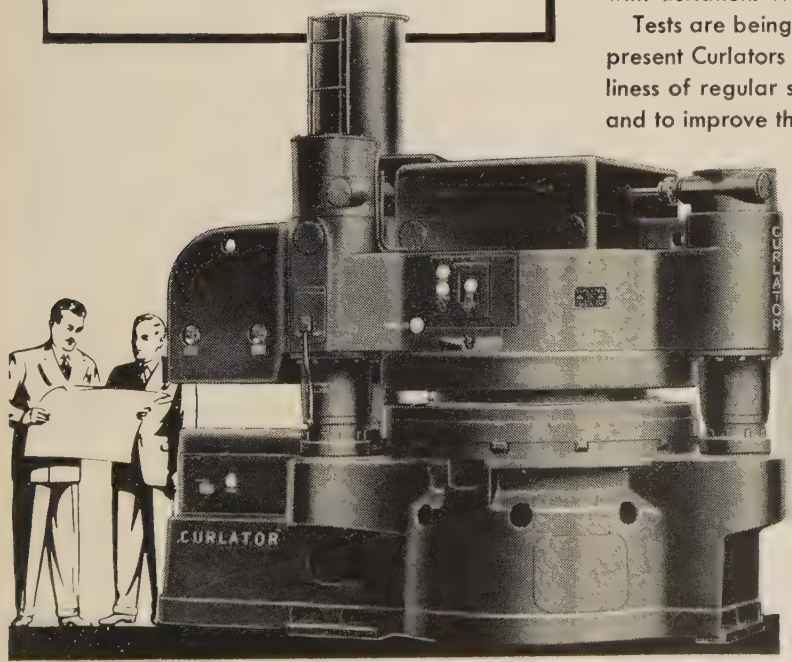
CURLATION is a new mechanical process for improving pulp properties, fully tested and thoroughly proved. Curlation not only produces a permanent change in the shape of pulp fibres, but also exerts a powerful de-shiving action, with negligible change in freeness.

CURLATION MAY BE ABLE TO *Save* 10% OF YOUR WOOD

Yes, Curlation may be able to save 10% of your wood, if you operate an unbleached sulphite mill. Curlators now in commercial operation on newsprint sulphite are making possible the manufacture of sulphite pulp of equal quality to that previously produced, with a saving of 10% in wood plus substantial savings in coal, limestone and sulphur. You, too, may be able to cut costs with Curlation. Why not investigate?

Tests are being conducted on new applications of Curlation. At present Curlators are being used effectively to improve the cleanliness of regular sulphite, to increase the yield of news sulphite, and to improve the bending qualities of folding boxboard liner.



WRITE for new bulletin C-2 on the C-50 CURLATOR. Inquiries are invited.

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Corporation
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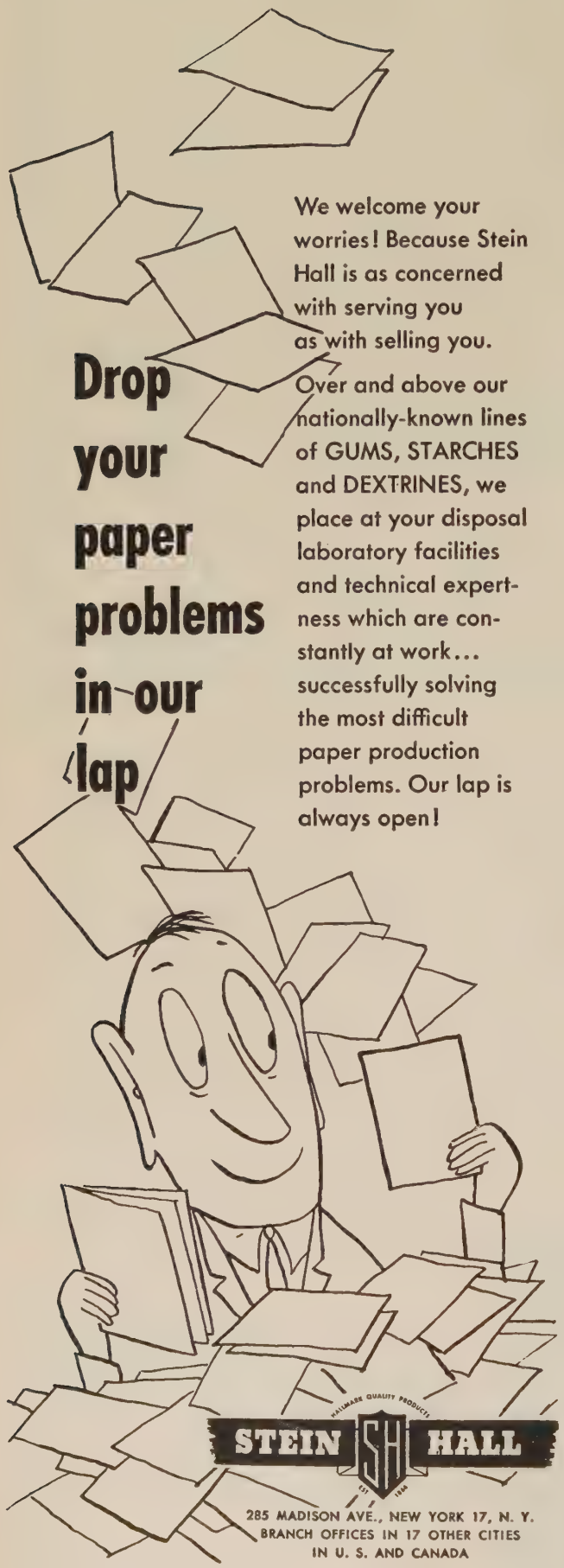
†T. M. Reg.—Curlator Corporation, Rochester, N. Y.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5. Flexibility at Low Temperatures (Including Coating Materials, Tapes, Laminated Products, etc. (Project 275)
6. Heat Sealability (Project 331)
7. Review of Assigned Tests (T-446, 448, 463, 464, 465, 474, 475, 477 and 806)
8. New Projects

2:00 p.m. PULP TESTING
L. V. Forman, Institute of Paper Chemistry, Appleton, Wis., Chairman
1. Dirt in Pulp T 213 m-43 (Project 140)

Meeting of Thursday, September 14

9:00 a.m. WAX TESTING (*Continued*)

9:00 a.m. PULP TESTING AND MICROSCOPY
1. Dirt in Pulp T 213 m-43 (Project 140)
2. Certain Aspects of Fiber Composition of Paper T 401 m-42 (Project 335)

9:00 a.m. PACKAGING MATERIALS TESTING (*Continued*)

9:00 a.m. GRAPHIC ARTS
Fred D. Elliott, Time-Life Laboratories, Springdale, Conn., Chairman
1. A brief report on the major grades of papers, their principal end uses, and percentage of the various grades printed by each of the three printing processes.
2. Discussion of the important physical characteristics needed by a given sheet to perform and print properly when run by the letterpress, gravure, and offset processes. (The purpose of this discussion is to obtain an opinion on what the papermaker should be testing in a sheet being manufactured for a specific type of press or method of printing.)
3. Review and discussion of various existing tests pointed toward studying their suitability for determining characteristics considered important in (2).
4. Discussion of new and not generally accepted tests such as the Brush-surface analyzer for surface-smoothness determinations.
5. Discussion of means of checking certain important characteristics for which there is no present adequate tests, such as the effect of capillarity or pinholes in paper on ink penetration or how to determine the water solubility of coated-offset paper.

9:00 a.m. CHEMICAL METHODS
Milton Fillius, Eastman Kodak Co., Rochester, N. Y., Chairman
1. The distillation step in the method for the determination of pentosans in pulp and wood
2. Methods for the moisture determination of pulp
3. Alternate subject—A rapid method for the determination of nitrogen

12:30–2:00 p.m. LUNCHEON (RECREATION BUILDING CAFETERIA)

2:00 p.m. OFFICIAL TOUR OF PAPER, COATING, AND FILM DEPARTMENTS OF THE EASTMAN KODAK CO.

Meeting of Friday, September 15

9:00 a.m. WAX TESTING (*Continued*)

9:00 a.m. MICROSCOPY
C. E. Brandon, Howard Paper Mills, Dayton, Ohio, Chairman
1. Discussion of the proposed revision of T 401 m-42 (Fiber Composition of Paper).

(a) The differentiation of alpha-treated softwood sulphite and highly bleached sulphite with the C-stain
(b) The effect of curlating on the C-stain
(c) General discussion of T 401 m-42 and of any new stains

9:00 a.m. PAPER TESTING
A. K. Warner, Skinner & Sherman, Inc., Boston, Mass., Chairman
1. Machine Direction of Paper T 409 m
2. Thickness and Density of Paper T 411 m
3. Bulking Thickness of Paper T 426 m
4. Ink Absorption of Blotting Paper T 431 m
5. Water Absorption of Bibulous Papers T 432 m
6. Water Absorption of Non-Bibulous Papers and Paper Board T 441 m
7. Specks and Spots in Paper T 445 m
8. Bursting Strength of Paper T 403 m
9. Pin Holes in Paper

9:00 a.m. NONFIBROUS MATERIALS TESTING (*Continued*)

9:00 a.m. PULP TESTING
1. Laboratory Processing of Pulp T 200 m-45 (Project 132)
2. Forming Handsheets for Physical Testing of Pulp T 215 m-45 (Project 333)

12:30–2:00 p.m. LUNCHEON (RECREATION BUILDING CAFETERIA)

2:00 p.m. WAX TESTING (*Continued*)

2:00 p.m. MICROSCOPY
1. Discussion of the revision of T-8 (Species Identification of Wood and Wood Fibers)
2. The use of the microscope in analyzing for mineral fillers in papers
3. Tests for elemental sulphur in pulp and paper

The following tests may be discussed in part with the Pulp Testing Committee on Thursday morning:
1. The Measurement of Fiber Length
   (a) Optical Method of the Eastman Kodak Co., Laboratory
   (b) Routine Method of the Alton Box Board Co., Laboratory
2. Discussion of a method for "The Determination of the Amount of Dirt in Pulp (Revision of T 213 m-43)"

2:00 p.m. CHEMICAL METHODS
1. The bleach consumption of pulp. A discussion of three TAPPI methods: T 214, Permanganate Number of Pulp; T 219, Bleach Requirements of Pulp; and T 202, Chlorine Consumption of Pulp.
2. The chemical analysis of papers containing wet-strength resins. A discussion of the complications introduced into the analysis of paper for alpha-cellulose, copper number, etc., by the presence of wet-strength resins.

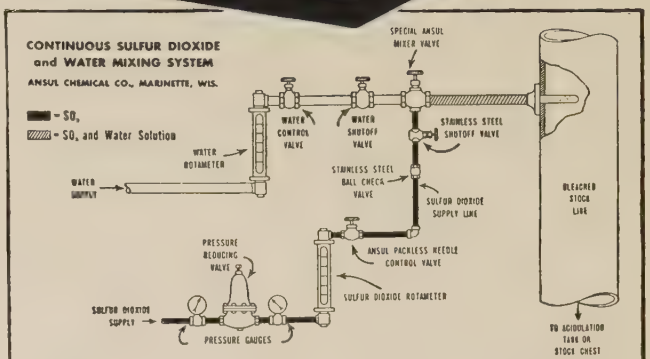
2:00 p.m. NONFIBROUS MATERIALS TESTING (*Continued*)

2:00 p.m. PULP TESTING
1. Specific External Surface of Pulp T 226 sm-46 (Project 334)
2. The Zero Span Test Applied to Pulp
3. Other Pulp Testing Methods

Note: The entire Testing Conference is informal. The aforegoing schedule approximates the program but it is subject to change depending on the special interest of those present.

FOR PERMANENT MAXIMUM *Brightness* in Bleached KRAFT Pulp

. . . INSTALL AN ANSUL Constant SO_2 Concentration System . . . and get Positive Control of Acidulation



This Ansul System provides a continuous metered flow of sulfur dioxide and water solution at any desired concentration and rate of flow.

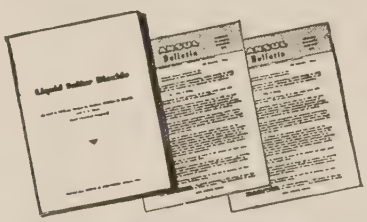
The solution may be introduced into the pulp at the acidulation tank, stock chest, the stock line from a washer, or at any suitable point in the bleaching system.

Ansul sulfur dioxide is an inexpensive acidifying agent . . . thoroughly efficient, and perfectly suited to the acidulation step in the preparation of bleached kraft pulp.

Ansul sulfur dioxide improves brightness and prevents color reversion because it:

1. Reduces colored ferric compounds to the soluble ferrous state so they may be easily washed from the pulp.
2. Bleaches and brightens the pulp by adjusting the pH to the acid side.
3. Acts as anti-chlor to remove residual chlorine and thus prevents formation of oxy-cellulose which would age to yellow compounds.
4. Permits dissolving of organic lime compounds so they may be removed by washing.

WRITE THE ANSUL TECHNICAL STAFF FOR FURTHER INFORMATION



Write today for these bulletins:
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PERSONAL MENTION

Items About New and Old Tappimen

New TAPPI Members

Edward C. Berg, Chief Engineer and Designer, Ace Carton Corp., Chicago, Ill.

Maximo Bunzl, Director, Bunzl & Biach A.G., Papierfabbriken Ortmann, Vienna, Austria, a 1935 graduate of the University of Vienna with a Ph.D. degree.

Robert D. Carter, Plant Chemist, Keyes Fibre Co., Waterville, Me. Attended Harvard University.

Harry E. Cluxton, Plant Manager, West Carrollton Parchment Co., West Carrollton, Ohio.

Harry F. Dean, Manager, Technical Div., St. Anne's Board Mill Co. Ltd., Bristol, England, a 1914 graduate of Bristol College with an M.S. degree, and a Ph.D. degree in 1923.

Gerrit G. De Haas, Chemist, Weyerhaeuser Timber Co., Longview, Wash., a 1942 graduate of the Polytechnic University, Zurich.

Arthur A. Deutsch, Assistant Chief Chemist, Container Corp. of America, Chicago, Ill.

Lauri I. L. Durchman, Engineer, American Defibrator, Inc., New York, N. Y., a 1911 graduate of Technische Hochschule für Handel & Gewerbe, Germany.

Edward R. Erb, Chief Chemist, Paulsboro Mfg. Co., Fullerton, Pa., a 1932 graduate of Pennsylvania State College.

Wm. F. Gerrow, Jr., Chemical Engineer, Fulton Bag & Cotton Mills, Atlanta, Ga., a 1949 graduate of Institute of Textile Technology with an M.S. degree.

Paul L. Gilmont, Research Chemist, Crossett Lumber Co., Crossett, Ark., a 1938 graduate of Massachusetts Institute of Technology, with a Ph.D. degree in 1940.

Hans Gunther, Director and Technical Manager, Gemeinschaft Papiersackindustrie E.V. and Vereinigung Natronpapiere E.V., Wiesbaden, Germany, a 1925 graduate of Strassburg College, Berlin.

Gordon G. Halvorsen, District Manager, Dicalite Div., Great Lakes Carbon Corp., Cleveland, Ohio, a 1938 graduate of University of Minnesota.

A. Lyman Hatfield, Technical Service Engineer, B. F. Goodrich Chemical Co., Cleveland, Ohio. Attended Ohio Wesleyan University.

Hans Th. Kiær, Managing Director, And. H. Kiær & Co. Ltd., Fredrikstad, Norway, a 1914 graduate of Royal Technical Institute, Dresden.

Charles F. King, Technical Director, United States Printing & Lithograph Co., Cincinnati, Ohio, a 1930 graduate of University of Illinois.

William A. MacCrehan, Jr., Vice-President in Charge of Quality, Empire Box Corp., Garfield, N. J., a 1942 graduate of Massachusetts Institute of Technology, with an M.M.E. degree from Harvard University in 1946.

Donald R. MacKinnon, Student, University of Maine, Orono, Me.

Murray MacNaughton, Trainee and Tester, Alliance Paper Mills Ltd., Merritton, Ont., Canada, a 1949 graduate of Trinity College, Oxford.

Yim Ngan, Controleur des Eaux et Forets, Service des Eaux et Forets du Cambodge, Phnom Penh, Cambodge.

Sam H. Popovich, Student, New York State College of Forestry, Syracuse, N. Y.

Jean C. Petit, Graduate Student, Columbia University, New York, N. Y., a 1947 graduate of Brussels University with an Sc.D. degree.

Robert O. Ragan, Chief Chemist, Chicago Carton Co., Chicago, Ill., a 1938 graduate of the Institute of Paper Chemistry.

Denis Roberts, Technical Superintendent, Courtaulds (Canada) Ltd., Cornwall, Ont., Canada, a 1923 graduate of University of London.

Urs Sieber, Manager, Cellulosefabrik Attisholz A. G., Post Luterbach So., Switzerland. Attended Institute of Technology, Darmstadt.

Manning A. Smith, Associate Professor, Bucknell University, Lewisburg, Pa., a 1937 graduate of Swarthmore College, with a Ph.D. degree from Massachusetts Institute of Technology in 1940.

Robert T. Smith, Research Chemist, Mosinee Paper Mills Co., Mosinee, Wis., a 1949 graduate of Purdue University.

Omar H. Somers, Quality Control Engineer, Western Printing & Lithographing Co., Poughkeepsie, N. Y., a 1933 graduate of Massachusetts Institute of Technolgoy.

Roger Uzac, Technical Director, Papeteries de Stenay et Pouilly, Paris, France, a 1926 graduate of Institut du Pin.

Kalevi Vesterinen, Chemical Control Engineer, Quebec North Shore Paper Co., Baie Comeau, P. Q., Canada, a 1940 graduate of Finland Institute of Technology, and a 1949 graduate of New York State College of Forestry.

Alvin R. Wilson, Chemist, Newark Paraffine & Parchment Paper Co., Newark, N. J., a 1950 graduate of Stevens College.

Ernest H. Wyche, Technical Service, Lukens Steel Co., Coatesville, Pa., a 1931 graduate of University of North Carolina.

TAPPI Notes

Daniel O. Adams is now Chief Chemist of the Research Division, Bird & Son, Inc., East Walpole, Mass.

J. H. Ainsworth, formerly Technical Director of the Mobile Paper Mill Co., is now Resident Manager, Sangamon Paper Mills, Inc., Eaton, Ind.

Francis O. Boylon, formerly Superintendent of the Tissue Div., Crown Zellerbach Corp., is now Asst. Resident Manager, Pacific Mills Ltd., Ocean Falls, B. C.

Everett F. Carman, Consulting Chemist has moved from Montclair, N. J., to 53 Randolph Place, West Orange, N. J.

James E. Foote, formerly of E. B. Eddy Co., is now General Manager, Pulp & Paper Division, Diamond Match Co., Plattsburg, N. Y.

Mark E. Fretz, formerly of the Detroit Sulphite Pulp & Paper Co., is now Research Chemist, J. M. Huber Corp., Huber, Ga.

Raimbault De Montigny, formerly of the Rolland Paper Co., Ltd., is now Techical Director, E. B. Eddy Co., Ltd., Hull, P. Q.

C. Lee Dryden, Manager of the Dryden-Harlan Electric Co., has moved his office from Appleton, Wis., to Milwaukee, Wis.

Martin J. Galbraith is now Technical Director, Sutherland Paper Co., Kalamazoo, Mich.

Pekka R. Haarla, formerly a student at the New York State College of Forestry is now a trainee at the Haarla Pulp Co., Tampere, Finland.

L. W. Heard, formerly a Consultant is now with the Longview Fibre Co., Longview, Wash.

Lester F. Herman, formerly Sales Engineer with the Fulton

Iron Works is now with the Gruendler Crusher & Pulverizer Co., St. Louis, Mo.

Elmer F. Hinner is now General Manager, Virginia Cellulose Dept., Hercules Powder Co., Wilmington, Del.

John C. Hyatt, formerly a student at the New York State College of Forestry is now Technical Trainee, for the Rhinelander Paper Co., Rhinelander, Wis.

Richard J. Krueger, formerly a student at the New York State College of Forestry, is now a production trainee, Sorg Paper Co., Middletown, Ohio.

Edward J. Meier is now a Sales Technician, Paper Chemicals Dept., American Cyanamid Co., Chicago, Ill.

Arthur J. Melbardis, formerly Engineer for Paper & Industrial Appliances, Inc., is now Engineer for the St. Marys Kraft Corp., New York, N. Y.

Perry J. Ostberg, formerly of the Jaite Co., is now with Ostberg & Diedrichs A/B.

Robert W. Ramsdall of Penick & Ford Ltd., Inc., has transferred from the Cedar Rapids to the New York Office. He is located in Medfield, Mass.

John H. Rich, formerly Production Manager, Plastic Film Corp., is now Asst. to the Vice-President in charge of Production, Riegel Paper Corp., Milford, N. J.

Sven A. Salmonson, 907 Terminal Sales Bldg., Portland, Oreg., is now sales and service representative of Chemical Linings, Inc., as well as Chemipulp Process, Inc., both of Watertown, N. Y.

Surrey W. Slater, formerly of Hearst Enterprises, Inc., is now Consultant, Pulp and Paper Mill Management, Lufkin Texas.

Robert W. Wagner, formerly student at the University of Cincinnati, is now Asst. to the Pulp Mill Superintendent and Chemist, Mead Corp., Sylva, N. C.

Alvin R. Wilson, formerly student at the Stevens Institute of Technology, is now Chemist, Newark Paraffine & Parchment Paper Co., Newark, N. J.

Sampson W. Yates, formerly of the National Folding Box Co., is now Production Manager, Robertson Paper Box Co., Montville, Conn.

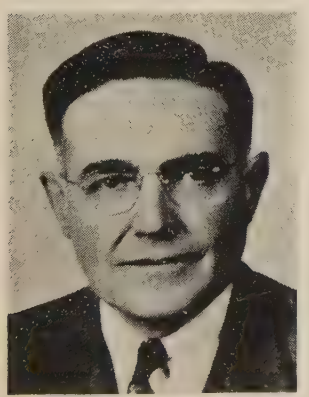
Nelson R. Yorke, formerly of the Panelyte Div., is now Chief Engineer, St. Regis Paper Co., Kalamazoo, Mich.

Harold F. Zigmund, formerly student at the New York State College of Forestry, is now trainee, Mosinee Paper Mills Co., Mosinee, Wis.

George A. Zinkil, formerly of the Container Corp. of America is now Special Representative for the Central Fibre Products Co., Chicago, Ill.

* * *

Clark C. Heritage has been named director of development for the Weyerhaeuser Timber Company, according to a recent announcement by J. P. Weyerhaeuser, Jr., president. Heritage will establish headquarters in the company's Tacoma general offices on September 1.



Clark C. Heritage

In 1937, Mr. Heritage organized development for the Wood Conversion Company of Cloquet, Minnesota, a Weyerhaeuser affiliate engaged in the manufacture of wood-fiber products. When the Weyerhaeuser Timber Company established development as a separately managed activity in 1941, Mr. Heritage was selected to construct facilities at Longview, Washington. He has directed the development work for both companies since that date.

Checked the finish on your paper lately?

Are you getting the finish you need to combat competition? Has your paper the quality that reflects superior calendering . . . gives it added sales appeal?

Many of America's leading paper mills standardize on Butterworth Calender Rolls for smoother, better quality finishing. We believe that the results obtained from only one of our rolls placed in your calender stack will convince you of their superiority.

You'll get increased production too. With Butterworth Calender Rolls you get many extra hours of top-flight service. Lose less labor time making changes.

Butterworth Calender Rolls are made of the finest materials available, to exact specifications. Pretested for strength, hardness and density before delivery.

We make calender rolls for all types of calendering in every size to your specifications. We can also refill your present rolls.

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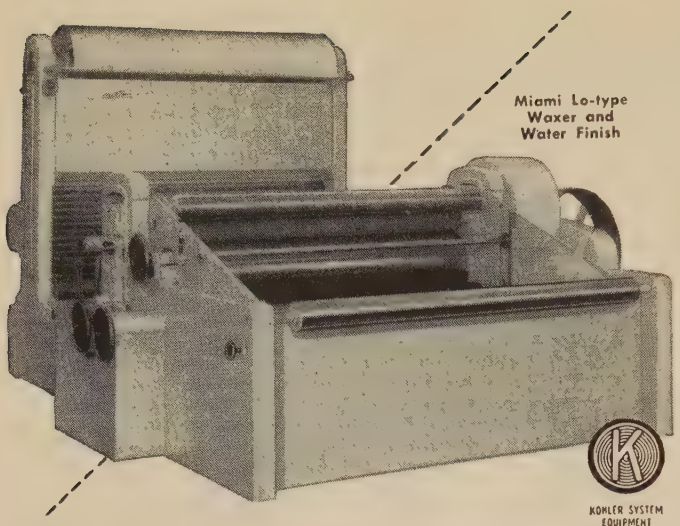
Butterworth Calender Rolls



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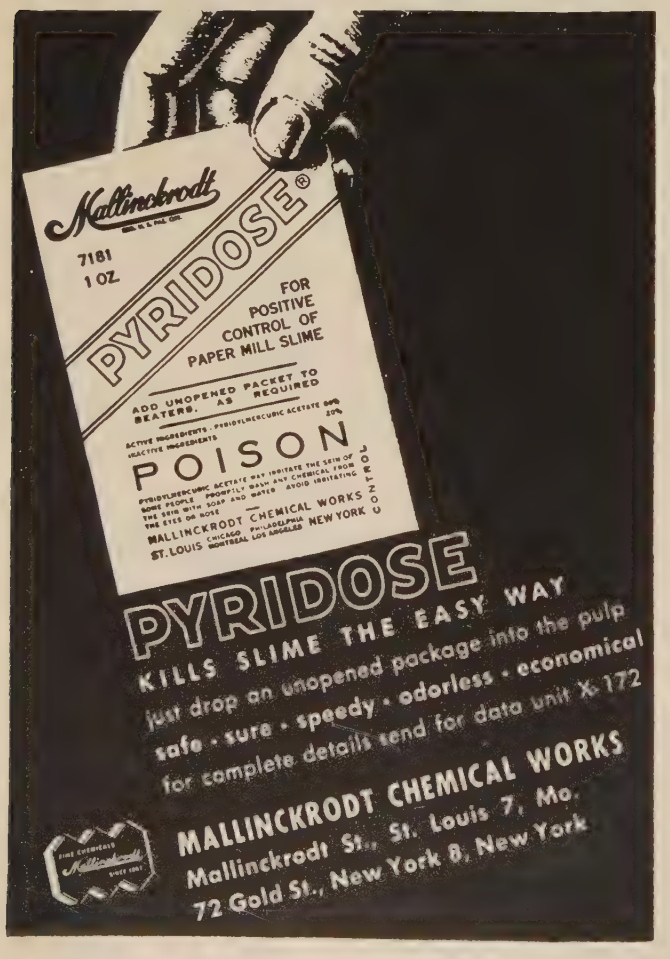
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In his new position, he will devote his full time to the Weyerhaeuser Timber Company.

New products and corresponding processes and equipment developed under Heritage's direction include fiber boards, both decorative and structural, fiber blanket, felt for construction and for industrial conversion, and bulk fiber for thermal insulation applied by pneumatic felting in place.

A new phenolic resin made it possible to produce low-cost, high-quality exterior grade plywood and a new resin extender accomplished further major improvement. When Weyerhaeuser built its first wholly-owned plywood plant, the development department contributed the barking, drying, gluemaking, and laminating operations.

Products from Douglas-fir bark were pioneered under the trade name of Silvacon. These are finding many industrial uses, both in the plants of customers and in those of Weyerhaeuser. Many varieties of whole wood fiber are going into industrial and building markets as Silvacel and Silvawool.

With an educational background of science at the University of Chicago and engineering at Armour Institute of Technology, Heritage has been in the production, sales, engineering, development, and management phases of organic chemicals and forest products for many years. He was one of the first to manufacture synthetic phenol and served for an extended period as chief of engineering design and development for National Aniline and Chemical Co., Buffalo, N. Y.

A few years later he directed the pulp and paper work of the Forest Products Laboratory of the U. S. Forest Service at Madison, Wis. Prior to Association with Weyerhaeuser, Heritage organized development for the Oxford Mills. He has specialized in the technology of forest products and in the incorporation of the development function in business organization.

Professionally, Mr. Heritage served as president of the Technical Association of the Pulp and Paper Industry from 1934 to 1936.

* * *

Ernani C. Da Costa is now the official corporate representative in TAPPI of Cia. Industrial de Papel Pir hy, Rio de Janeiro, Brazil.

J. F. Butterworth has succeeded J. C. Dean as representative of the Socony Vacuum Oil Co. in TAPPI.

* * *

Ethyl Corp. has removed its office in New York from 405 Lexington Ave. to 100 Park Ave. *Harry Kuhe* represents the Ethyl Corp. in TAPPI.

* * *

The Improved Paper Machinery Co. has removed its New York office from 441 Lexington Ave. to 230 Park Ave. *John H. Noble* is located at this address.

* * *

The Spencer Chemical Co. has appointed Harold A. Ford as industrial sales representative. He will devote his attention to development work in the ammonium bisulphite wood-pulping process. Mr. Ford was formerly with Du Pont in Wilmington.

Industry Notes

The Beloit Iron Works, Beloit, Wis., has underwritten the first scholarship for the new University of Maine Pulp and Paper Foundation. The General Dyestuff Corp., New York, has become the first company member.

* * *

The Brown Co., Berlin, N. H., is supplying tree-planting stock to its pulpwood suppliers, on a tree for tree basis. A producer supplying the Company with 500 cords of pulpwood will be entitled to 4000 trees.

* * *

Under the European Recovery Program a 35,000 metric ton sulphate pulp mill will be built at Cacia, Portugal. It will be operated by Companhia Portuguesa de Celulose. 8500 tons will be bleached.

* * *

Paper and board production in the United States during May amounted to 2,040,678 tons. This is the highest production for any one month on record and reflects an increase of 32% over production in May, 1949. Domestic production of newsprint at 88,930 tons is the highest for any postwar month.

* * *

The Union Bag & Paper Corp., is now supplying waxed paper bags to publishers for individual wrapping of newspapers to be delivered to homes in rainy weather. The open end can be twisted to keep out water. The bags are printed with the name of the newspaper. The wax employed has a melting point of 128–130 amp.

* * *

Foresters estimate that nature plants 75 billion trees each year in the U.S.A. Forests cover a larger proportion of New England than any other comparable region in the United States. Christmas tree sales bring $100,000 in cash income into New Hampshire every year. Forest fires consume 14% of wood growth in Southern forests each year, exceeding the total amount cut for pulpwood. With every Southern state stressing good forest management the golden age of forestry is just beginning in the South.

* * *

The Brown Co., Berlin, N. H., has completed its installation of 52 Hooker-type electrolytic cells. These cells replace 400 of the old type cells and produce the same amount of chlorine and caustic soda with substantial reduction in floor space and in the amount of electricity required.

* * *

The Federal Security Agency, Public Health Service, Division of Water Pollution Control, Washington 25, D. C., has issued a Guide to Source Material on Water Pollution Control (May, 1950).

* * *

The New York State College of Forestry, Syracuse, N. Y., has issued a bulletin on "Spruce Canker."

* * *

Armstrong Machine Works, Three Rivers, Mich., has issued a new bulletin on "Air Traps."

* * *

The J. M. Huber Co., New York, N. Y., will complete a 30 million-pound furnace carbon black plant at Baytown, Texas, by March 1, 1951. The Company is a large producer of clays and printing inks.

* * *

The James T. Flannery Co., Jersey City, N. J., has been appointed Eastern Sales Representative to the paper and plastic fields. Mr. Flannery is President of the National Association of Waste Material Dealers.

* * *

The Chemical Plants Div., Blaw-Knox Co., will build a large new chlorine and caustic soda plant at Saltville, Va., for the Mathieson Hydrocarbon Chemical Corp. The plant is expected to be in operation in 1951 and will be one of the most modern in the United States. The design will be based on the Mathieson mercury cell process, which produces chlorine and rayon-grade caustic soda of 50% concentration directly from the cells. Demand for the product continues to increase and

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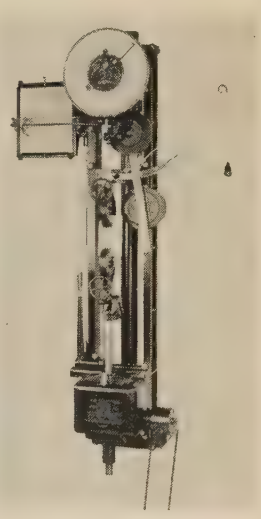

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it is probable that additional production units of this type will be built as the chlorine industry expands.

* * *

The Westinghouse Electric Corp., will employ more than 300 engineering graduates this year. George D. Lobingier, manager of student recruitment indicates that although graduating classes have created a temporary excess of engineers, industry will be faced with a shortage of qualified engineers by 1953.

* * *

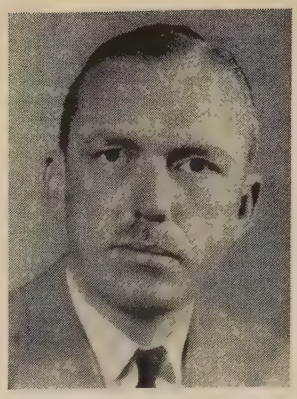
A new drive for installation on a 72-inch wide supercalender which will produce a double finish on waxed paper at pushbutton-controlled speeds up to 1600-f.p.m., has been ordered from the Westinghouse Electric Corp., by the Appleton Machine Co. The supercalender will be installed at the Peshtigo, Wis., mill of the Badger Paper Mills, Inc. Of particular interest is the motorized wind-up stand used with this supercalender. A booster generator provides "inch" operation of this section, stalled tension, IR drop compensation, and inertia compensation.

* * *

E. D. Powers has been elected Vice-President of the American Cyanamid Co. He will be in charge of all matters concerning plant operations.

* * *

The Paper Chemicals Dept., Industrial Chemicals Div., American Cyanamid Co., 30 Rockefeller Plaza, New York 20, N. Y., has issued a new 18-page booklet on "Quality Advantages Gained with Alwax and Waxine Sizes." It includes a survey of treated paper, listing more than 150 grades of paper and paperboard. It recommends size to be used.



Harold A. Ford

Henry K. Benson

The Spencer Chemical Co., Kansas City, Mo., announces the retention of Dr. Henry K. Benson of Seattle, Wash., as consultant, specializing in the development of the ammonium bisulphite process for wood pulping. Dr. Benson was Professor of Chemistry at the University of Washington for 43 years. He is now Professor Emeritus and Research Consultant. Dr. Benson was one of the organizers of the TAPPI Pacific Section.

The Spencer Chemical Co., which has recently become a member of the Technical Association of the Pulp and Paper Industry has, according to John R. Riley, Jr., General Sales Manager, been challenged by the advantages offered to the wood-pulping industry by the ammonium bisulphite process, but many questions remain unanswered. In obtaining the services of Dr. Benson it is hoped that much progress, of benefit to the industry will be made.

The Spencer Chemical Co., with plants at Pittsburgh,

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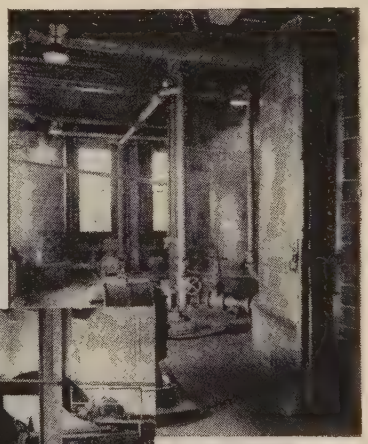

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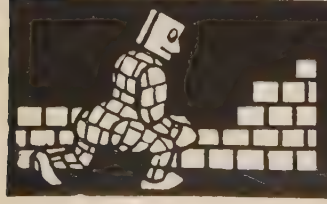

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Kan., Henderson, Ky., Chicago, Parsons, Kan., and Charlestown, Ind., will soon become the country's largest producer of nitrogen products from natural gas. The Company has issued an interesting booklet on "Chemicals for Industry and Agriculture."

* * *

The Atlas Mineral Products Co., has issued a new General Bulletin MCC No. 1 which describes the Atlas line of chemical construction materials, including corrosion-proof linings and cements, acid-proof brick and tile, corrosion-proof protective coatings. It includes handy estimating data. This may be obtained from the company at 42 Walnut St., Mertztown, Pa.

* * *

The General Dyestuff Corp., has moved its Chicago office and laboratory from 731 Plymouth Court to 310 West Polk St.

* * *

The Glyco Products Co., 26 Court St., Brooklyn, N. Y., announces that its new spreading agent, Paraspred, for paraffin and microcrystalline waxes is now in commercial production. In addition to its spreading properties it plasticizes paraffin wax, improving its adhesiveness. It also improves penetration of wax into porous materials such as paper. Samples may be obtained from the Company.

* * *

General Electric sectional-drive equipment will replace an old electric-drive system on the No. 2 machine of the P. H. Glatfelter mill at Spring Grove, Pa. The new drive will allow an increase in production speed from 700 to 1000 f.p.m. Complete coordination of all sections from the couch, through the presses, driers, calenders, and reel will be maintained at all speeds by the electronic-amplidyne control. In addition, paper tension will be controlled through the use of a paper tensiometer, a new G. E. development.

* * *

The Hercules Powder Co., Wilmington, Del., has introduced a new defoamer which is available in 2½-lb. bricks. A brick of Defoamer 4 will make about 40 gallons of a final dispersion at 0.75% solids. Twenty bricks, enough for 800 gallons of dispersion, are packaged and shipped in a corrugated container which can be stored in a small amount of space. Very small quantities of the emulsion are said to control most foam conditions encountered in papermaking systems. The emulsions are very stable, thereby eliminating the need for continuous agitation during use.

* * *

The Farrel-Birmingham Co. Inc., Ansonia, Conn., has issued a new 12-page Bulletin No. 117 on "Farrel Paper Machine and Board Calenders." Concise descriptions are given of design features.

* * *

The Westinghouse Electric Corp., Box 2099, Pittsburgh 30, Pa., has issued a new 16-page booklet B-4038 highlighting new drives for some of the major machines involved in paper finishing and converting. It describes in detail modern drives for supercalenders, winders, coaters, and corrugators. The new Westinghouse type AV packaged adjustable-speed drive is described for such applications as sheet calenders, waxers, tubers, bag machines, double facers, and combiners and pasters.

* * *

The Cameron Machine Co., 61 Poplar St., Brooklyn, N. Y., has issued a Bulletin 4002 describing the new Cameron "PG" slitter grinder. The unit can handle either large 4½-inch

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Use the versatile Oakite Gun for wet-steam rinsing of soured wires after cleaning; for removing grime from cylinder wires; for desliming save-alls. Other suggested uses for the Gun are given in specially prepared 28-page Paper Mill Maintenance-Cleaning Handbook. A FREE copy will be gladly mailed on request. Send to address below today!

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Single Instrument Measures Smoothness, Porosity and Softness of Paper

You just interchange the lower test plates in the GURLEY-HILL S-P-S Tester to convert it into an instrument for testing either smoothness, porosity or softness of any type of paper, by measuring a given air-leakage over or through the paper.

This 3 in 1 laboratory "assistant" is simple to operate, quick and accurate, and a real utility instrument where printing quality of paper must be reliably measured.

Bulletin No. 1400 describes the S-P-S Tester as well as other Gurley paper testing instruments. It's worth writing for today. W. & L. E. Gurley, Station Plaza & Fulton Sts., Troy, New York.

mill-type wheels or the smaller 3-inch wheels. The grinder is approximately 24 by 12 by 15 inches and has a heavy base to absorb vibration.

* * *

Paul E. Burchfield has been appointed director of technical service Wyandotte Chemicals Corp., Michigan Alkali Division, Wyandotte, Mich.

Left:
Paul E. Burchfield

Right:
John S. Johnson

Mr. Burchfield succeeds John S. Johnson who has been director of technical service since 1939. After receiving his doctorate from Western Reserve University in 1934 Dr. Burchfield joined the Harshaw Chemical Co., as a research chemist. He joined Wyandotte in 1943 and spent his first three years as asst. supervisor of the chemical engineering department, research division. In 1946 he was appointed asst. director of the technical service department. In his new capacity, Dr. Burchfield will continue his active contacts with the pulp and paper and the chemical industries.

* * *

Anyone concerned with the packaging or shipping of products will be interested in the new San Joaquin Division of Fibreboard Products Inc., which is just getting into full production near Antioch, Calif. This plant, Fibreboard's fifteenth on the Pacific Coast, will add 250 tons daily capacity to the company's present daily output of over 750 tons of paperboard for packaging purposes.

Air view of new San Joaquin Division of Fibreboard Products Inc., located near Antioch, Calif.

Of added interest is the fact that this plant is making much-needed packaging materials largely from what previously has been the waste of logging, lumbering, and boxmaking activities of California. The plant has two gigantic paperboard machines; one making Tuf-Fir, a nine-point corrugating material the other producing bleached kraft for making food cartons of many types.

All the wood chips used for the nine-point corrugating materials are from wood waste formerly burned by sawmills, box mills, and planing mills. Likewise, a large portion of the wood chips for making the bleached kraft are made from fir trees that are unsuitable for lumber. Much of it is cut under a scientific conservation program for a perpetual timber supply on the 75,000 acres which Fibreboard recently purchased as a major source of raw material for the San Joaquin Division operations. This acreage lies in Placer, Nevada, and Sierra Counties adjacent to Truckee, Calif., with Hobart Mills as headquarters for logging operations.

This new plant is part of a 10-year plant-betterment program starting in 1946, involving capital expenditures of upward of fifty million dollars.

Fibreboard's San Joaquin Division pulp and board mill is unusual for a number of reasons.

First of all, it is said to be the first plant to make nine-point corrugating material out of a 100% coniferous wood.

It is the only kraft mill, either semikraft or standard kraft, in California.

The San Joaquin Division mill was planned and constructed under the direction of N. M. Brisbois, Vice-President of Fibreboard Products Inc., and Leland S. Rosener, Consulting Engineer, San Francisco. Swinerton & Walberg were the general contractors.

The main building is 1000 feet long and 200 feet wide. It is built of structural steel and reinforced concrete. Three G-E 5000-kva. turbine generators develop the entire electrical energy for the plant. The exhaust from these turbines provides the steam for the process of reducing the chips to usable cellulose fibers.

This new Division of the company is providing new jobs for about 700 people.

Heading the roster of key personnel at the San Joaquin Division is C. R. P. Cash, newly appointed Manager, succeeding C. M. Stitt, who becomes Manager of Fibreboard's new Central Engineering Division.

Incorporated in 1927, and jointly controlled by The Paraffine Companies, Inc., and Crown Zellerbach Corporation, Fibreboard has become one of the three largest producers and converters of paperboard packaging materials in the United States. D. H. Patterson was president until last December when he resigned that position, but remains as a member of the board of directors. He was succeeded in the presidency by T. N. Bland, formerly vice-president and general manager. R. E. Bundy is Vice-President in Charge of Production.

OBITUARY

Samuel Lattimore Foster

Sam Foster, Chief Engineer for the Kalamazoo Vegetable Parchment Co., Parchment, Mich., died on July 2.

Mr. Foster was born at Starkville, Miss., on June 27, 1887 and graduated from Mississippi State College as a mechanical engineer in 1910, following which he spent another year at Cornell University.

In 1910 he joined the International Paper Co., at Glens Falls, N.Y., receiving his apprentice training at the Palmer Falls mill and the Bureau of Tests in Glens Falls. From 1911–1912 he was resident engineer at the Ticonderoga mill and from 1912–1930 at the Rumford, Maine, mill. At the latter he was mill manager from 1930–1935.

In 1936 he became resident manager of the Hudson Falls, N. Y., mill of the Union Bag & Paper Corp., and in 1937 became production manager of the Sandy Hill Iron & Brass Works at Hudson Falls.

Samuel Lattimore Foster

He joined the Kalamazoo Vegetable Parchment Co. organization in 1944 as chief engineer. Since joining KVP he enjoyed the ambition of every engineer, that of building a new mill, the KVP mill at Espanola, Ont., and the new plant of the Appleford Paper Products Ltd., at Hamilton, Ont.

During the past few years Mr. Foster has taken an active interest in the Engineering Division of the Technical Association of the Pulp and Paper Industry and has been esteemed by his fellow engineers because of his sound common sense and willing participation in the discussions relating to the division's interests.

He is survived by his wife Elma Adelaide (Poe), his son Arthur, a paper machine engineer at the Mobile Div., of the Southern Kraft Corp., his son Sam Lattimore, plant engineer at the same mill, and son Paul, accountant at the KVP Espanola mill, a daughter Aldelaide (Mrs. Clay Hearon) at Starkville, Miss., and a daughter Vivian (Mrs. Edward Huntoon) at Marlette, Mich.

Interment was in Starkville, Miss.

TAPPI DIVISIONS AND COMMITTEES

Recent Reports of Activities

Acid Pulping Committee

John McEwan, Pulp Division, Weyerhaeuser Timber Co., Everett, Wash., has succeeded George H. McGregor of the Minnesota & Ontario Paper Co., International Falls, Minn., as chairman of the Acid Pulping Committee. Following Dr. McGregor's resignation as chairman it was decided to establish the nucleus of this Committee on the Pacific Coast where interesting progress is being made relative to the sulphite pulping process. The Pacific Section was requested to organize and sponsor the committee.

Associated with Dr. McEwan at the present time as members of this committee are:

R. I. Thieme, Soundview Pulp Co., Everett, Wash.
E. O. Ericksson, Puget Sound Pulp and Timber Co., Bellingham, Wash.
K. G. Booth, Central Research Dept., Crown Zellerbach Corp., Camas, Wash.
F. J. Weleber, Publisher's Paper Co., Oregon City, Ore.
E. H. Woodruff, Rayonier, Inc., Port Angeles, Wash.

In addition to the aforegoing Dr. McGregor has been asked to organize a Lake States Subcommittee and L. C. Beighey of the Hammermill Paper Co., Erie, Pa., has been asked to organize an Eastern Subcommittee. Each group will work on problems of interest to their respective regions. The West Coast Group will deal with special bases and waste liquor, the Lake States Subcommittee with resinous woods and the Eastern Subcommittee with hardwoods.

Several research projects have been suggested by committeemen. The first is a study of the equilibrium concentration of sulphur dioxide over ammonium bisulphite solutions for various values of combined sulphur dioxide, temperatures, and partial pressures of sulphur dioxide over the solution. This study may be extended to cover magnesia solutions also.

Another study being considered deals with the calculation of absorption coefficients for sulphur dioxide in ammonia and magnesia solutions for various tower packings, such as 6 and 3-inch spiral tile, 2-inch Berl saddles, Reschig rings, partition rings, etc.

Another pair of related projects that have been suggested are an investigation of methods of determining the solids content of sulphite waste liquor. Present methods of solids determination of the sulphite waste liquors give different answers depending on the drying or solvent extraction conditions. It is possible that an absolute solids determination cannot be found. If so, an evaluation of present methods would be of value in establishing an empirical method upon which to base specifications. A study of the viscosity of different base liquors at different temperatures and solids content should be valuable for piping layouts, evaporator design for systems in which the waste liquor is evaporated or burned.

TAPPI Standards T 629 m-48 (Analysis of Sulphite Waste Liquor) and O 406 p-48 (Standard Terms Used in the Sulphite Pulping Process) are being reviewed.

Alkaline Pulping Committee

The Alkaline Pulping Committee is deviating its attention, at present, to the preparation of its Fall Conference to be held at Jacksonville, Fla., on Oct. 25–27, 1950. A feature of this meeting will be a visit to the Hudson Pulp and Paper Co. mill at Palatka, Fla., on October 27.

This meeting will be a revival of the unusually fine conferences held earlier at Savannah, New Orleans, and Asheville. It will be the first conference held under the Committee Chairmanship of Henry Vranian of the Chesapeake Corp West Point, Va., who succeeded Kenneth G. Chesley, as Chairman.

Associated with Mr. Vranian as members of the Alkaline Pulping Committee are the following:

K. D. Running, Halifax Paper Co., Roanoke Rapids, N. C. *Secretary.*
P. B. Borlew, Container Corp. of America, Fernandina, Fla.
K. G. Chesley, Crossett Paper Mills, Crossett, Ark.
G. L. Clark, Coosa River Paper Co., Coosa Pines, Ala.
L. V. Forman, Institute of Paper Chemistry, Appleton, Wis.
R. R. Fuller, Gulf States Paper Corp., Tuscaloosa, Ala.
J. J. Goss, Gaylord Container Corp., Bogalusa, La.
K. M. Guest, National Container Corp., Jacksonville, Fla.
E. A. Harper, Hudson Pulp & Paper Co., Palatka, Fla.
W. F. Holzer, Crown Zellerbach Corp., Camas, Wash.
W. P. Lawrence, Champion Paper & Fibre Co., Hamilton, Ohio.
C. C. Porter, Southland Paper Mills, Lufkin, Texas.
N. F. Robertson, Cellulose Engineers, Tacoma, Wash.
E. E. Rodabaugh, New York and Pennsylvania Co., Lock Haven, Pa.
R. H. Stevens, National Container Corp., Jacksonville, Fla.
M. L. Taylor, Union Bag & Paper Corp., Savannah, Ga.

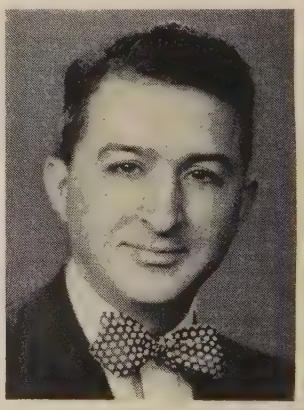
The Committee is having an annotated bibliography of alkaline pulping prepared at the Institute of Paper Chemistry by S. D. Wells. Mr. Wells has prepared a number of these bibliographies in the past. This work is financed by the Southern Pulp and Paper Manufacturer.

A Subcommittee on Testing Procedures was authorized at the annual meeting. It was brought out in discussion that the methods used in the various mills are at considerable variance and need to be reviewed for the purpose of establishing methods that will produce results that can be understood in all of the mills manufacturing kraft pulp. Messrs. Porter, Borlew, and Rodabaugh were appointed as members of this committee.

At a meeting of the Committee held in April, plans were made for the Alkaline Pulping Conference to be held in the fall. E. A. Harper was appointed Chairman of the Local Arrangements Committee. He will be assisted by Karl Guest of the National Container Corp. R. R. Fuller of the Gulf States Paper Corp., was appointed Chairman of the Program Committee.

Although a special full day trip to the mill at Palatka, Fla.

John McEwan Chairman, Acid Pulping Committee



Henry Vranian Chairman, Alkaline Pulping Committee

has been made a main feature of the program a cordial invitation has been received from the Container Corp. of America and Rayonier, Inc., at Fernandina, Fla., the St. Marys Kraft Corp., at St. Marys, Ga., and the National Container Corp. at Jacksonville, Fla., for members of TAPPI to visit their mills during the week of the meeting.

The preliminary technical program of the Conference as indicated by Mr. Fuller includes the following topics:

A. *Causticizing Operations*
   1. Review of the literature on theoretical aspects of the causticizing reaction and effects of variables on plant operations.
   2. Effect of chemicals present on the causticizing reaction.
   3. Chemistry of the sulphur compounds and the control of sulphidity at the causticizing plant.
   4. Effect of sulphidity on operations.
   5. Centrifugal clarification of white liquor.
   6. Operation of causticizing equipment.
   7. Discussion of the causticizing operation.

B. *Lime Burning*
   1. Review of the theoretical aspects of lime burning in rotary kilns.
   2. Lime kiln operation.
   3. Economics of lime kiln operation.
   4. Case studies of lime burning operations at mills.
   5. Discussion of lime kiln operations.

C. *Miscellaneous Topics*
   1. Pressure washing.
   2. Oxidation of black liquor.
   3. Refining of kraft pulp.
   4. General discussion of kraft mill operating problems.

All technical sessions will be held at the George Washington Hotel, Jacksonville, Fla. Room reservations should be made through Frank Winchell, Manager of the Jacksonville Tourist and Convention Bureau, Hemming Park, 307 Hogan St., Jacksonville, Fla.

Pulp Purification Committee

The Pulp Purification Committee is devoting all of its efforts to the preparation of a much needed book on "Pulp Bleaching." The separate chapters are being written by a large number of members, all of whom are recognized authorities in their respective fields. The publication, when it is issued, will be the most up-to-date and comprehensive of its kind ever prepared.

This work is being carried on by the members of the Pulp Purification Committee and a few invited specialists. The personnel of this committee is as follows:

W. D. Harrison, Riegel Paper Corp., Milford, N. J., *Chairman*
P. E. Burchfield. Wyandotte Chemicals Corp., Wyandotte, Mich.
Ferri Casciani, Niagara Alkali Co., Niagara Falls, N. Y.
F. P. Doane, Sandy Hill Iron & Brass Works, Hudson Falls, N. Y.
V. P. Edwardes, Consultant, Cornith, N. Y.
L. V. Forman, Institute of Paper Chemistry, Appleton, Wis.
Emil Heuser, Retired, La Jolla, Calif.
R. P. Hill, Pulp Bleaching Corp., Seattle, Wash.
E. F. Hinner, Virginia Cellulose Dept., Hercules Powder Co., Wilmington, Del.
Ferdinand Kraft, Marathon of Canada Ltd., Marathon, Ont.
R. L. McEwan, Buffalo Electro-Chemical Co., Buffalo, N. Y.
W. H. Monsson, Hooker Electrochemical Co., Niagara Falls, N. Y.
J. H. Noble, Improved Paper Machinery Co., New York, N. Y.
F. W. O'Neil, New York State College of Forestry, Syracuse, N. Y.
R. K. Prince, Allis-Chalmers Mfg. Co., Milwaukee, Wis.
J. S. Reichert, E. I. duPont deNemours, Niagara Falls, N. Y.
John Schuber, Solvay Sales Co., Syracuse, N. Y.
F. A. Simonds, Forest Products Laboratory, Madison, Wis.
Vernon Woodside, Mathieson Chemical Co., New Orleans, La.

R. S. Hatch, Consultant, Monterey, Calif., has been appointed Editor of the book on bleaching and is working on the first six chapters which have been completed.

The committee, in discussing the chapter on "Special Bleaching Agents" have decided to include chlorite, chlorine dioxide, zinc hydrosulphite, peracetate, peroxide, permanganate, ozone, ultraviolet light, and catalysts. This chapter has been assigned to A. H. Nadelman, Professor of Pulp and Papermaking at Western Michigan College, Kalamazoo, Mich.

L. A. Moss, Technical Director of the Whiting Plover Paper Co., Stevens Point, Wis., will prepare the section on Rag and Cotton Bleaching of the Miscellaneous Fiber Bleaching Chapter.

The Association and the industry is much indebted to the members of the Pulp Purification Committee for undertaking this very important project. As progress is made further reports will be published.

Mechanical Pulping Committee

Fred W. O'Neil, Associate Professor of Pulp and Paper Manufacture at the New York State College of Forestry, Syracuse, N. Y., succeeded R. M. Drummond of the International Paper Co., Glens Falls, N. Y., as Chairman of the Mechanical Pulping Committee.

At present Professor O'Neil is reorganizing the committee personnel with the thought in mind of dealing largely with what may be called groundwood specialty operations in contrast to the large-scale newsprint groundwood operations. In view of the rapid progress being made in the United States in the field of specialty grinding and the semichemical pulping operations that are closely related to groundwood production it is felt that there is a need to have special attention given to these new and changing operations.

One of the Men Behind Eastwood Wires

Chester Mankiewicz

Here we show a fine-wire drawing machine being threaded or "strung up." The finished sizes are going through their final drawing in a special lubricant and coolant, then onto spools for use as warp or shute wires.

What began as a one-foot length of heavy wire may "wind up" as a 2,200 foot length of fine 80-mesh wire size.

Expert supervision is employed to control the coolant and to maintain the diamond dies so that they will draw to a tolerance of .0001 inches—another example of the precision required to produce top-quality fourdrinier wires.

EASTWOOD-NEALLEY CORPORATION • Belleville, N. J.

Corrugated Containers Subcommittee

The Corrugated Containers Subcomittee held its organizational meeting at the office of the Container Corp. of America, 10 North Clark St., Chicago, Ill., on June 20, 1950. Those present were:

F. D. Long, Container Corp. of America, Chicago, Ill., *Chairman.*
P. Johnson, Cornell Wood Products Co., Milwaukee, Wis.
W. S. McDonald, International Paper Co., Georgetown, S. C.
B. Mendlin, Cornell Wood Products Co., Milwaukee, Wis.
C. H. Olmstead, American Boxboard Co., Grand Rapids, Mich.
M. L. Taylor, Union Bag & Paper Corp., Savannah, Ga.
R. G. Young, Ohio Boxboard Co., Rittman, Ohio.

Mr. Long opened the meeting by describing the various existing TAPPI committees relating to containers, pointing out that in the existing structure many potential TAPPI members in the corrugated box field, as well as many present, TAPPI members, have felt that insufficient attention had been paid to the field of corrugated container fabrication. As a result of this need, a short meeting was held at the last annual TAPPI meeting to determine whether there was sufficient interest to support and make successful a committee devoted exclusively to considerations of the problems involved in fabrication of corrugated containers. Inasmuch as TAPPI already has a Containers Committee, it was considered appropriate that the proposed new committee should be a Corrugated Containers Subcommittee working somewhat independently, but under the over-all guidance of the Containers committee.

Committee Scope

Before proceeding to a determination of other details of the committee's setup and functioning, Mr. Long pointed out that it would be necessary to define the scope of the committee and read excerpts from letters he had received relative to the committee's scope in response to his letter of June 12. The opinions expressed by these letters, as well as the consensus of the meeting, relative to the scope of the new committee, were that, for the time being, the committee's activities should be limited to the practical, as well as technical, aspects of manufacturing corrugated containers, with specific emphasis on improvements in machinery, design, and methods of operation. It was pointed out by one of the members present that, by comparison with other portions of the paper industry, the development of equipment for corrugated box manufacture had been relatively insignificant for the past 25 years and that some of the thinking inspired by the committee's activities may be useful in producing real progress in this direction. It was agreed that emphasis should be placed on studies of manufacturing methods and equipment common to all the various raw materials used for corrugated boxes, and that we should avoid work directed toward a comparison or evaluation of different fibrous raw materials.

Committee Name

In selecting a name for the committee, it was pointed out that considerations of brevity and completeness are both important in naming a committee and that, in general, a compromise is necessary. Among the more promising committee names suggested were: TAPPI Corrugated Fabrication Committee and TAPPI Corrugated Container Committee. In view of the fact that the committee setup is actually that of a subcommittee rather than a separate committee, and that the term "Corrugated Containers" permitted a broader definition of committee functions as long as they related to corrugated containers, it was decided to recommend use of the name TAPPI Corrugated Containers Subcommittee.

Committee Membership

Mr. Long introduced this subject of membership pointing out that, in selecting the group for the organization meeting, he had attempted to give representation to all of the major manufacturing groups in the industry, including users of semichemical, straw, kraft, and jute materials. This basis for selection of committee membership appeared reasonable to the group, and it was recommended that it be used in setting up the permanent committee. Before proceeding to a detailed discussion of the actual make-up of the committee, considerable attention was devoted to a discussion of the most desirable size for the committee. It was pointed out that, in the interests of efficient committee operation, particularly since a major part of the work is handled by correspondence, it is desirable to work with a relatively small committee consisting only of active members. The small group, of course, has yet another advantage both in matters handled by correspondence and by meetings, in that it is much easier to arrive at a committee decision with a small group than with a large group. On the other hand, it was felt that there are advantages to a large committee in that it is possible to recognize and include even a relatively large number of people if they are interested in participating actively in the committee. In order to obtain the advantages of both large and small committees, the group recommended that the Corrugated Container Subcommittee become a steering committee for the corrugated container field to guide and coordinate the activities of individual subcommittees assigned to specific problems with chairmanship by individual members of the steering committee. The chairmen of the subcommittees for individual problems would then be expected to handle, with the aid of a committee appointed by themselves, the collection of data and the organization of panel discussions or other types of programs for regular TAPPI meetings.

In selecting the committee membership, it was believed that the greatest unity of purpose would be obtained if it were possible to make up both the steering committee and the individual problem subcommittees from men who are actively engaged in either a technical or operating capacity in the actual manufacture of corrugated boxes. This should not be understood to mean, by any means, complete exclusion of representatives of suppliers, but it was felt that the committee activities should be substantially by and for the box manufacturers. It is true, of course, that all of us have close and valued contact with suppliers, and it is felt that much of the supplier's know-how and data can be utilized more constructively for their benefit and that of the industry if the committee activities are kept free from any suspicion of bias for or against a particular manufacturer's products.

Based on the above considerations, the following individuals were selected as members of the TAPPI Corrugated Containers Subcommittee (Steering Committee as described above).

F. D. Long, *Chairman,* Container Corp. of America, 10 N Clark St., Chicago, Ill.
L. K. Burnett, *Secretary,* Ohio Boxboard Co., Rittman, Ohio.
P. Johnson, Cornell Wood Products, Milwaukee, Wis.
M. F. Knack, River Raisin Paper Co., Monroe, Mich.
W. B. Lincoln, Inland Container Corp., Indianapolis, Ind.
J. R. Little, Hinde & Dauch Paper Co., Sandusky, Ohio.
W. S. McDonald, International Paper Co., Georgetown, S. C.
W. K. Tobin, American Boxboard Co., Grand Rapids 2, Mich.
H. T. Scordas, Union Bag and Paper Corp., Savannah, Ga.

Although all of the men on the above list had expressed interest, either directly or through their representatives, in participation in the Corrugated Containers Subcommittee

activities, none of those present on June 20 felt like volunteering for the important post of Committee Secretary. Accordingly, it was decided to fill this position by lot from among the names selected for the Steering Committee, and L. K. Burnett was chosen secretary.

Committee Problems

Following decisions on organizational matters and the scope of the committee as described above, suggestions for fabrication problems to be worked on by the committee were considered. It was decided for the time being to concentrate on problems relating to the combiner proper since the existence of so many problems relative to this equipment is generally apparent, and because improvements at the combiner may be expected to cause or make possible improvements in subsequent operations by supplying a better combined board. The principal problems for committee activities suggested were:

1. Flute contours (A and C probably the most important)
2. Corrugator roll wear
3. Starch adhesives
4. Silicate adhesives
5. Control of heat and moisture at the combiner
   a. Warping
   b. Condensate removal
   c. Means of measuring heat transfer
6. Finger lines
7. Double backer adhesion
   a. Bonding
   b. Board damage
   c. Other problems
8. High and low corrugations

It is, of course, expected that other important corrugator problems, as well as problems peculiar to succeeding operations, will become apparent as time goes on, but it was believed that the above list is adequate to serve as a basis for committee activity in the immediate future.

It was agreed that, in the interest of having the best chance to have something to present at the February TAPPI Meeting, it would be desirable to select problems for immediate action on which some progress could be made in a short time. Following this line of thought, it was decided to appoint from the Steering Committee a subcommittee chairman for each of six of the above problems. It is hoped that each of the individual problem subcommittees can prepare a questionnaire in the next few weeks for submission to individual box plants to determine the importance of their problem in plant operations and to indicate what steps are taken to minimize and control the effects of troublesome conditions.

In view of the need for getting the committee work started at the earliest possible date, the following time table was agreed upon:

1. Each subcommittee chairman is to send a list of his subcommittee members to Mr. Long by July 15.
2. Preliminary drafts prepared by each subcommittee on its particular problem are to be sent to Mr. Long by August 15.
3. By September 15 it is expected that all of the questionnaires will have been submitted to the entire Steering Committee for comments by Mr. Long or Mr. Burnett and will have been returned for preparation and distribution to the industry.

Excluding Mr. Burnett, the Steering Committee secretary, who will be adequately occupied with general committee correspondence, the remaining members of the committee were assigned the chairmanship of committees to work individually on the problems as indicated below:

1. Starch adhesives, P. Johnson, Cornell Wood Products, Milwaukee, Wis.
2. Silicate adhesives, M. F. Knack, River Raisin Paper Co., Monroe, Mich.
3. Corrugator roll wear, J. R. Little, Hinde & Dauch Paper Co., Sandusky, Ohio.
4. Finger lines, W. R. Tobin, American Boxboard Co., Grand Rapids 2, Mich.
5. High and low corrugations, W. S. McDonald, International Paper Co., Georgetown, S. C.
6. Heat and moisture control on the combiner, H. T. Scordas, Union Bag and Paper Corp., Savannah, Ga.

Of the above problems, the first five are considered to be ones on which appreciable progress can be made for the New York meeting in 1950. With regard to the sixth problem, Mr. Long will approach Mr. Montgomery of the TAPPI Drying and Ventilating Committee relative to the possibility of utilizing some of the background gained in his investigations on paper machines to facilitate a study of this problem.

General

Mr. Long requested that copies of all committee correspondence be sent to him and to Mr. Burnett, the secretary.

In connection with the questionnaires, it was the consensus that all the questionnaires should be sent out by the committee secretary to the industry at one time under a single cover letter describing the committee and its aims, and soliciting individual companies' cooperation for the over-all good. Mr. Long will prepare a rough draft of such a letter, which he will submit to the subchairmen and which he wishes returned with comments along with the first draft of their subcommittee questionnaires.

As was indicated, it is planned for the secretary to send out and have returned to him all of the questionnaires. At a given date, or after a suitable number of questionnaires have been returned, the secretary will turn the answers to each questionnaire over to the proper subcommittee chairman for analysis. The subcommittees will then summarize the results from the questionnaire and return them to the secretary for distribution to all who contributed information.

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LOCAL SECTION ACTIVITIES

Reports of Meetings, Personnel and Events

Maine-New Hampshire and New England

The Maine-New Hampshire and New England Sections held a successful jointly sponsored meeting on June 23–24, 1950, at the Wentworth By-the-Sea, Portsmouth, N. H. with nearly 300 members and guests attending. The technical program featured the subject: "The Theoretical and Practical Aspects of Stock Refining" and was divided into two sessions held Friday afternoon, June 23, and Saturday morning, June 24.

Fiber Motions in Papermaking

Presiding at the Friday afternoon meeting was George A. Day, Brown Company, Berlin, N. H. who introduced S. G. Mason of the Pulp and Paper Research Institute of Canada as the first speaker. Dr. Mason discussed "Some Theoretical Aspects of Fiber Motions in Papermaking." Dr. Mason stated that when a suspension of fibers is pumped, stirred, or otherwise caused to flow, the resulting velocity gradients cause the fibers to undergo rotations. These rotations are of considerable importance in explaining screening action, flocculation, paper formation, etc.

The fibers in rotational and translational motion tend to collide when the consistency exceeds a certain value. This follows since each fiber in motion sweeps out a considerably larger volume than its actual volume; and, as the consistency is increased, the critical consistency or concentration is reached above which the fibers cannot undergo unimpeded rotations because of insufficient space. As can be seen in Table I, the critical concentration is directly related to the axis ratio of the fiber; the axis ratio being a function of the fiber dimensions, as defined below:

Table I

Axis ratio	*Critical concentration, g./100cc.*
20	0.125
30	0.055
40	0.031
50	0.020
60	0.014

$$\text{axis ratio} = \frac{\text{length}}{\sqrt{(\text{Width})\ (\text{thickness})}} \left(\frac{\pi}{2}\right)$$

An estimate of the order of magnitude of the collision frequencies in papermaking stocks can be illustrated by considering flow through a paper-machine slice. Assuming laminar flow and that the slice can be represented as two fixed parallel plane surfaces, Table II gives the minimum number of collisions per fiber per second that might be expected on a 228-inch fourdrinier machine operating at 1000 f.p.m. with a slice opening of 0.57 inch and stock discharge of 5500 g.p.m. For these calculations an axis ratio of 40 is taken with an effective bulk volume of 3 cc. per g., the computed number of fibers per gram being 1.1 by 10^7.

It is seen that the collision frequencies are surprisingly high, particularly at the higher concentrations.

The growth of independent aggregates by mechanical entanglement above the critical concentration is of importance with regard to the formation characteristics of paper. In stock around 0.5% consistency, fibers cannot exist separately unless there is a complete absence of shear motion.

In the headbox and slice, the suspension is subjected to shear by either a stirring action or forced flow. While this shearing action undoubtedly reduces flocculation resulting from interparticle attraction, it will not necessarily influence the intermeshing or mechanical clotting of the fibers which results from their tendency to rotate.

Table II

Consistency, %	*Minimum collision per fiber per second*
0.01	2.4
0.02	4.8
0.03	7.4
0.1	24
0.3	74
0.5	134

The tendency to clot mechanically will increase markedly as the axis ratio is increased. It will be aided further by fibrillation which enhances fiber interlocking and interweaving through large number of hooks protruding from the fiber and increased flexibility of the fiber. It is known that the increased fibrillation and flexibility resulting from beating has an adverse effect on sheet formation. It is suggested that this arises primarily from mechanical clotting and only secondarily from ordinary flocculation arising from interparticle attraction.

Regional Kraft Pulp Properties

The properties of sulphate pulps from various geographical locations, as revealed by laboratory evaluation, was the subject discussed by W. V. Torrey, S. D. Warren Company. All tests were carried out on handsheets, with no additives present. Five pulps from northern woods (Maine, New Brunswick, Quebec, Sweden, and Finland) exhibited family resemblances in their physical characteristics. More recently a pulp from Ontario wood was found to belong in this group also. They showed rapid development of bursting strength and attainment of a high maximum value. The family resemblance was continued in the similarity of the values for tear, folds, shrinkage, and slowness.

Officers of the Maine-New Hampshire and New England Sections of TAPPI. Seated, left to right: R. J. Proctor; G. A. Day; P. S. Bolton; A. E. Bachmann, President of TAPPI; J. L. Parsons; S. G. Mason, representing CPPA; R. G. Macdonald, Secretary of TAPPI.
Standing, left to right, J. P. Bainbridge, Jr., F. S. Klein, P. Gooding, H. T. Barker, A. G. Dries, H. E. Pratt, A. P. Gregory, W. F. Daniell, L. C. Jenness, and J. F. Wright.

Two southern and one west coast sulphate pulps were tested in the second group. Although these three pulps showed about the same shape of burst curves as the northern woods group, the numerical values were less. For northern pulps the average maximum strength value was 135, and this value for the second group was 115. The tearing strength closely resembled the northern group. The rate of development of folding endurance was similar with the three pulps, but their numerical values were less than those of the northern pulps.

There was a good agreement in the shrinkage tests for the two southern pulps but the spread between these and the value for the west-coast pulp was noticeable. It shows that the southern pulps hydrate at a considerably more rapid rate than the west-coast pulp. High shrinkage always accompanies a slow stock, and low shrinkage always goes with a free stock. Under the microscope the southern pulp fibers exhibited much more fibrillation and disintegration than those from northern woods. The beating tests were carried out in calibrated porcelain ball mills.

Pulp Properties and Chemical Constitution

Irwin B. Douglass, Department of Chemistry, University of Maine, discussed the properties of pulp as related to chemical composition. In the last analysis the properties of any pulp depend on the physical state of aggregation and the chemical nature of the substances that comprise that pulp. In recent years attention has been called to holocellulose, the total carbohydrate portion of wood, and the three types of material of which it is composed: i.e., true cellulose, cellulosans, and the polyuronide hemicelluloses. Modern pulping processes produce a material consisting chiefly of partially degraded true cellulose but also containing small quantities of cellulosans and polyuronide hemicelluloses. The last named components seem to be responsible for some of the important properties of pulp such as hydration and beatability.

Any consideration of pulp quality must be concerned with the chemical properties of the principal component, true cellulose. This long-chainpo lymer of glucose, in spite of a substantial degree of chemical stability, is sensitive to attack by hydrogen ions and oxidizing agents. A periodic re-examination of the fundamental organic reactions involved in such attack will lead to a better understanding of the effect of chain length on the viscosity of dissolving pulp and on the qualities of the finished sheet of paper.

The formula that best describes cellulose is that of an extremely long chain of glucose units in cyclic form held together by an oxygen atom bound to the first carbon of one glucose unit and the fourth carbon of the next residue. The number of such glucose residues bound together in a single cellulose chain is large and is known as the degree of polymerization or D.P.

The cellulose of a growing tree undoubtedly consists of molecules of widely differing chain length ranging from less than a D.P. of 100 to perhaps as high as 10,000. The D.P. of an unopened ball of cotton is about 5000; when the ball opens, weathering lowers the D.P. to about 3500. Alkaline pulps have fairly high average D.P., but those prepared by the sulphite process are lower. When the average D.P. falls to 100–125, cellulose loses its fibrous structure and turns to a friable powder. Long chain length gives high fiber strength.

The average D.P. of a cellulose sample tends to decrease with chemical treatment due to the fact that the oxygen bridge of the glucose units reacts with water, especially under the influence of hydrogen ions, with a resultant breaking of the chain at that point. If chains rupture near the ends, the fragments will be soluble in water and the yield of pulp will be decreased. As chains become shorter, solubility increases in 17.5% sodium hydroxide, and the alpha cellulose content is decreased. It is seen therefore that the sulphite process not only seriously lowers yield but reduces quality. Glucose units, however, are subject to chemical attack in other ways favored by alkaline conditions.

Oxidation bleaching with hypochlorites seriously attacks cellulose molecules. One of the virtues of newer bleaching processes is their failure to attack cellulose.

The hemicellulose in a pulp is responsible for rapid beating development of maximum burst, minimum opacity, and greaseproof properties. It is found that beating is most rapid at 26.5% hemicellulose and maximum burst occurs at 20%.

With mounting production costs any process which promises a higher pulp yield appears attractive. On the other hand, any appreciable increase in pulp yield can only be accomplished by less degradation of alpha-cellulose during the pulping operation or by the retention of more cellulosans and polyuronide hemicelluloses in the pulp. Because these latter substances are not identical to alpha cellulose, their inclusion in the pulp may alter markedly such properties as hydration characteristics and suitability for rayon manufacture.

The polyuronide hemicelluloses are of particular interest. These compounds are of unknown composition but from their carboxyl and pentosan content are believed to resemble certain other natural products suchas the gums and mucilages. Much excellent work on the fundamental side has been done on organic structure of these latter materials in recent years and we are coming to a much better understanding of their hydrophyllic character and amorphous structure.

Swelling and Shrinkage of Fibers

Wilfred Gallay, E. B. Eddy Company, Hull, Quebec, Canada, gave a stimulating discussion on the "Swelling and Shrinkage of Pulp Fibers in Relation to Papermaking and Paper Strength." A summary of Dr. Gallay's presentation is found in the following abstract:

"The degree of swelling of pulp fibers by water is a basic property of the fibers affecting beating, fiber deposition, and paper properties. Cellulose should be considered from this point of view in relation to thermoplastic synthetic resins and natural linear polymers, the properties of which may be varied over a wide range by the addition of plasticizers.

"The methods which have been used for measuring the degree of swelling of cellulose in water were reviewed, and the data compared. It would appear that considerable further research is required in the elaboration of a satisfactory method. The swelling value should afford an indirect measurement of the plasticity and flexibility of the pulp fiber. The effect of the degree of swelling of the pulp on resultant paper properties were discussed by the speaker, as was also the effect of drying and heating of pulp fibers on resultant swelling and paper strength. The relation between strength development during drying of the web and the drying and heating effects were reviewed."

Business Meetings

Following a discussion of the afternoon papers each Section met separately to conduct its annual business meeting. The Maine-N. H. Section elected George A. Day, Brown Company, Berlin, N. H. as chairman for the ensuing year. The vice-chairman elected was J. J. Thomas, S. D. Warren Company, Cumberland Mills, Me. and H. E. Pratt, Pejepscot Paper Company, Brunswick, Me. was re-elected secretary and treasurer. Newly elected members of the Executive Committee comprise Warren F. Daniell, Great Northern Paper Company, Millinocket, Me., Henry S. Hooper, Penobscot Chemical Fibre Company, Great Works, Me., T. E. Kloss, Hollingsworth & Whitney Company, Waterville, Me., and A. E. Jones, Oxford Paper Company, Rumford, Me. It was voted to hold the Fall Meeting on October 13 and 14 at Waterville, Maine, in conjunction with the official opening of the new Keyes Science Building at Colby College. It was also

The clam bake at Wentworth By-the-Sea

voted to consider a contribution to the University of Maine Pulp and Paper Foundation.

At the New England Section annual meeting, R. J. Proctor, Fitchburg Paper Company, Fitchburg, Mass., was elected chairman and Harold W. Knudson, Hollingsworth & Vose Co., E. Walpole, Mass., was made vice-chairman. A. G. Dreis, Hercules Powder Company, Holyoke, Mass., and H. T. Barker, Bird & Son, Inc., E. Walpole, Mass., were re-elected secretary and treasurer, respectively. Newly elected members to the Executive Committee comprise Samuel J. Quattrocchi, Deerfield Glassine Company, Monroe Bridge, Mass., W. C. Hunter, The New Haven Pulp and Board Co., New Haven, Conn., C. J. Backus, Whiting & Co., Holyoke, Mass., and Herbert Brawn, Keith Paper Company, Turners Falls, Mass. Plans were discussed for a National Coating Conference of TAPPI, scheduled for April 18–20, 1951 at the Hotel Statler, Boston, Mass. Arrangements will be made for the visitation of plants in the vicinity.

Social Events

During the first technical session the Ladies Bridge Tournament was held and the following prize winners were announced in the evening: First prize, Mrs. Laura Gregory; second, Mrs. W. H. Woods, third, Mrs. P. S. Bolton; and consolation prize, Mrs. W. L. Hinds.

At the conclusion of the dinner on Friday evening the officers of both TAPPI Sections were introduced. Representing the Technical Section of the Canadian Pulp and Paper Association was S. G. Mason of the Pulp and Paper Research Institute of Canada. National TAPPI representatives were R. G. Macdonald, Secretary-Treasurer, and A. E. Bachmann, President, who brought the greetings of the TAPPI officers. President Bachmann's prepared remarks follow:

"Mr. Chairman—Ladies and Gentlemen:

"I am very happy indeed to be here tonight to bring you the greetings of the Officers and Executive Committee of TAPPI. I am particularly glad to welcome the New England Section to a joint spring meeting with the Maine-New Hampshire Section at this beautiful place. The Maine-New Hampshire Section is one of our younger sections but nevertheless has, by the caliber of its meeting programs, already arrived at full equality with some of our best sections. We hope that your respective executive committees will see fit to continue this relationship in order that this meeting will continue to grow in importance as the result of the greater diversity and degree of subject matter available from the larger group.

"Your chairman asked me to discuss briefly the State of the Union pertaining to TAPPI. In general, and compared with the past, the state of TAPPI affairs is excellent.

"All our sections are holding regular meetings according to their general pattern, either one night meetings monthly or meetings of longer duration less often. Due to the generally high-grade and responsible leadership of the various sections, the caliber of their programs, and consequently their attendance, is continually improving. Many of the sections are turning into TAPPI headquarters detailed accounts of their papers and discussions thereby making considerable more valuable technical material available for publishing in *Tappi*.

"After a long process of editing, the TAPPI Routine Testing Methods are now in your hands. These routine testing methods we expect will be quite valuable as they show the details of testing methods used to actually control production, where for some reason the TAPPI standard methods are too long or need modification for the specific objective to be accomplished at the individual mill. The TAPPI standards methods are meticulously designed (and rightly so) for research rather than control where many different tests must be obtained in sufficient time to do something about it in the process. In addition, the routine test methods cover many specific quality properties which are only of interest to limited groups and on specific grades. They are naturally also of a tentative nature and are frequently modified from time to time, even by their originators, in the event that experience determines their unsuitability for the particular property they are designed to measure. Considerable time, however, is often expended by all of us to develop suitable routine methods to control our production. The gathering and publishing of these methods we expect will result in a considerable standardization of these within the time limits and degree of accuracy neccessary. This will result in the greater use of a common test language among interested groups to the extent that we will be enabled to discuss among each other more intelligibly some of the principles of papermaking. Until we standardize further than we have some of our operating tests, we will not get too far in any discussions of operating principles such as you for example are discussing at this meeting in that highly controversial subject of stock preparation.

"The Executive Committee fully recognizes that the gathering and publishing of this group of routine tests is just a start toward a program of continuous augmentation and standardization of such tests. To this end because of the excellent job done on gathering these by the sections, they have designated the future gathering of these as a sectional function. We hope your respective sections will form a routine testing methods subcommittee within your groups.

"The story about the TAPPI committees is about the same as usual. Our active committees are very active and a few need to be reactivated. The Fundamental Research Committee, one of our best, recently held an international symposium on Papermaking Properties of Fibers at Quebec in a joint meeting with the Canadian Technical Section. This meeting was extremely well attended by delegates and speakers from as far away as England and Australia. The interest of the group was sustained at an extremely high level as judged by the perfect attendance at the meetings and the length of the sessions.

"The Committees of the Engineering Division will again hold a conference this fall at Cincinnati. The Alkaline Pulping Committee will meet also this fall at Jacksonville. A meeting of special interest to this group should be the September meeting at Eastman Kodak in Rochester of the Committees of the Testing Division. Our Fibrous Agricultural Residues Committee will again hold a meeting this fall in the Middle West. The Plastics Committee also will hold a meeting at Syracuse in October of this year. We also expect to hold a meeting this summer of the newly formed Cost Engineering Committee at Sheldon Springs, to develop a program of activity for this committee. We will be glad to hear from anyone who is interested in this subject and wishes an invitation.

"The membership continues to grow and now has reached a total membership of about 4300 individual members. Our magazine has now attained a degree of maturity and stabilization and has universally good acceptance by members and advertisers. In order to retain this membership TAPPI must continue to expand its activities to meet the diversified interests of this large membership.

"An almost limitless opportunity for diversified expansion of TAPPI activities lies in work of our various Paper Manufacturing Committees. The meetings of these groups over the years have literally only scratched the surface of the subject matter and data available. While the meetings held on this subject have been the object of extreme interest on the part of a large proportion of our membership, they have, however, produced but little in the form of settled or semisettled principles. We must change our tactics from this unrelated fragmentary approach to a concerted attack on specific objectives. Certainly the development of the atomic bomb was not accomplished by a chipping off of fragments of knowledge, but rather by an assignment to specific teams of specific objectives on individual phases of the over-all problem. Also certainly, despite the fact that papermaking contains a great many variables, the resolution of papermaking phenomena to coordinated principles, from which application to specific situations can be made, is somewhat short of the immensity of the task confronting the developers of the atomic bomb.

"We have tried over the years many organizational approaches to enlist not the interest (we always had that as demonstrated by

attendance at meetings), but rather the enthusiasm for cooperative working together on these problems. The development of papermaking principles is not like individual pieces of research which can be accomplished by individuals working alone. Because of the necessarily practical limitations of the individual's job and the rigidities of equipment, raw materials and grade patterns which form the boundaries of his intimate knowledge, no one individual or no one company thoroughly understands the basic principles of the broad papermaking field. Naturally, we do not expect to accomplish such an objective within a few years because of limitations of time and lack of availability of data. We can, however, make a start in this direction by individuals volunteering or accepting assignments to chase down in collaboration with other members possessing common interests a phase of this important subject matter.

"In an effort to make a start in this direction, we expect to try this summer to gather enough material from various members of the Executive Committee and others to get an illustrative example of the tentative principles on a specific phase of paper manufacture. We have chosen for this effort, the subject of Pulp Characteristics, including methods of testing and their interpretation in terms of paper quality properties and operating results. We would be more than pleased to have anyone in the audience who wishes to participate in such a composite paper to write me at once, or if that involves overcoming too much inertia, at least accept an assignment which we think might be helpful in the project.

"Technical men of today are relatively fortunate. The technical man of today is not merely tolerated as a fad to be dispensed with at the first signs of depression. Due to unprecedentedly long sustained excellent business conditions, most companies have enlarged their technical organizations many fold. The technical organization has had a chance of long enough duration to fully demonstrate its worth. As a result, Management today is extremely conscious of the necessity for organizing for continuous improvement in the form of Control Systems Development, Administration of Quality Control, Quality Improvement, Cost Reduction, and Research. To a large degree the technical organization has been intrusted with the full responsibility for the Improvement Function.

"Technical men and technical organizations alike have been materially assisted in their individual contributions to technical achievements by the TAPPI literature. Certainly the bleaching of kraft, to name only one of our foremost developments of modern times, owes its fruition to much of the fundamental research literature published by TAPPI thereby enabling each subsequent investigator to profit by the work done before his. Organized collaboration on the common knowledge of the principles of our industry is one of the prime functions of TAPPI as an association. The association, however, is only as good as the individual members make it by taking an active part in its programs and contributing their mite to the general stream of knowledge and experience. I urge you all to take a more active part in the affairs of some of the TAPPI committees in which your prime interests lie, to the end that TAPPI as an association will continue to merit even more increasingly the active support of the management of our industry."

Entertainment by Hum and Strum, radio and television singing stars, and dancing concluded Friday's program of events.

Refining Equipment

The Saturday morning technical session covered the practical aspects of stock refining and P. S. Bolton, Robert Gair Co., Uncasville, Conn., was moderator at the panel discussion. Nine representatives of refining-equipment manufacturers described the construction, operation, and performance of their respective machines.

The use of a Downingtown Pulper for disintegrating wet broke was demonstrated by means of a motion picture, presented by R. W. Polleys, Downingtown Manufacturing Company, Downingtown, Pa.

The Sprout-Waldron No. 36-2 single rotary-disk refiner, with a 42-inch disk, was described by Thaxter W. Small, Jr., representative of the Sprout, Waldron and Company, Muncy Pa. This type of refiner, with a 200 to 450-horsepower motor, at 900 r.p.m., has been employed in a variety of pulping applications, such as, for neutral sulphite semichemical chips, insulating board, sulphite and kraft knot and screen rejects, groundwood tailings, bull-screen rejects, hot stock refining (kraft pulp), bleached soda pulp, and waste paper. The machine is designed to provide a rubbing and brushing action

Enjoying the clam bake are more of the group.

on chips, knots and fiber bundles. Its function is diameter reduction (defibering), not length reduction.

The Sprout-Waldron refiner is available in three models: standard, semi-acid resistant, and fully-acid resistant. Power requirements vary from 2–4 hp.-days per ton for prerefining kraft pulp to 28–35 hp.-days per ton for groundwood tailings. The construction of the equipment was detailed by the speaker and numerous examples were cited of its use in the industry.

In a paper entitled "Modern Stock Treatment," Roy N. Johnson, of the Shartle Brothers Machine Company, Middletown, Ohio, stated that modern stock preparation systems are designed to perform (1) pulping, (2) defibering, (3) fibrillation, (4) cutting or any part of these four functions. The proportion of each is dependent entirely on the type of paper required and the type of furnish used. Although many mills producing their own pulp do not have pulp-distintegrating equipment, some integrated mills, as well as nonintegrated mills, have installed hydrapulpers or breaker beaters to convert the pulp into flowable form for further treatment.

The Hydrafiner is an efficient defibering machine. Three factors are involved in developing stock strength without cutting the fibers: relative effect of horsepower vs. speed, stock consistency, and inlet pressure. The Hydrafiner should be operated at a relatively high speed vs. horsepower. The optimum consistency figure is 6% and an inlet pressure of about 10 p.s.i. for this machine. These factors insure the development of maximum strength with minimum cutting.

Fibrillation in the Hydrafiner results in increased tear, burst, and shrinkage, with a slight drop in freeness. The ideal Hydrafiner setting would result in a bar to bar clearance which could be expressed in terms of fiber diameters.

A well-formed, closed-up sheet requires the cutting of fibers which can be performed by the jordan. Three factors promoting this operation are: relatively high horsepower vs. speed, consistency (3–3½%), and no inlet pressure above that required to keep the jordan full.

The speaker emphasized the value of a centralized control system which makes it possible for the operator to control the process within the limits required for successful operation. The Duocontrol was described as equipment which can be preset for desired current or power value and will automatically maintain this setting irrespective of stock consistency, freeness, or inlet power conditions for the duration of the refining cycle.

The principle of Dynomizing was discussed by G. A. Peterson, Rice, Barton Research Corporation, Worcester, Mass., who described the types of machines utilizing this principle: Dyno Pulper, Quatro Pulper, Dyno Chest, and Dyno Finer. These machines have in common one or more Dyno Pellers,

Part of the group at the Maine-New Hampshire-New England clam bake.

which are concave disks studded with hard carbide particles. The revolving disk creates a suction which draws hydraulically the stock to its center and then centrifugal force forces the stock across the carbide particles under pressure and high velocity, setting up a vigorous circulation within the container. This action is termed "Dynomizing." In this manner pulp, waste paper, and wet-strength papers are defibered, and their characteristics further developed.

The horsepower required for defibering and completely separating the fibers on dry waste paper stocks is approximately 4 hp. per day per ton defibered. On kraft pulp the horsepower requirement is about the same as for waste paper and on soda or sulphite pulp it ranges from $^1/_2$ to $^3/_4$ of the above figure.

In the event that slushing the stock only is required, the above figures would be cut approximately in half.

These machines are ideally suited for handling all types and classes of paper and pulp and are sized for producing both small and large tonnages. They are also designed to take care of broke as it is made on the paper machine without further handling or as a central unit in the finishing room. They will produce a high quality of completely defibered stock on which each fiber is separated from its neighbor without cutting or shortening the fiber and with no appreciable drop in freeness.

The Sutherland Refiner was described by Lionel M. Sutherland, Sutherland Refiner Corporation, Trenton, N. J. This machine embraces both a continuous beating and refining system. The assets of this refiner are: (1) rapid burst development, (2) high-tear retention, (3) equal burst at higher freenesses resulting in faster drainage, thus permitting increased machine speeds and higher production, (4) less wet and dry broke, therefore less rehandling of broke and more net tonnage, (5) parallel operation permitting greater flexibility in stock preparation and rapid changes in grades and sheet characteristics, and (6) a minimum of cutting.

The Jones Pulp-Master was described by Charles B. Muzzy, E. D. Jones and Sons Company, Pittsfield, Mass., as a pulper for the disintegration of baled raw material. Built in four sizes, 500, 1000, 2000, and 4000 pounds, it will reduce a bale of pulp within a short time to defibered slush at better than 6% consistency. Normally arranged for batch operation, the Pulp-Master can be made to discharge continuously.

The No. 1 Jones Refiner was suggested by the speaker as suitable equipment for clearing fiber bundles from a waste paper mixture for a board filler, or other low-grade sheet. This is a jordan-type machine which can be connected in series to produce a continuous flow of prepared stock from the slush stock storage chest to the paper machine.

The Fibremaster is a refining machine recently produced by the Jones Company. It has about twice the capacity of the No. 1 Refiner and can be used as a jordan or as a refiner in either a continuous or a recycling system.

The Jones recycling system, making use of two separate stock tanks, is automatic in operation. The procedure will repeat itself through the refiner until the desired characteristics of the stock are obtained.

For the preparation of high-quality papers the Jones Bertrams Beater was recommended. Slides were shown explaining its construction. In comparing the refining recycling system with the Betrams beater, there are important advantages favoring the latter, such as, greater flexibility of treatment, higher efficiency, better control, higher consistency stock, and no pump for stock circulation.

The Morden Stock-Maker, according to S. T. Orton, Jr., Union Machine Company, Fitchburg, Mass., is primarily a beating machine capable of delivering on a continuous basis papermaking fibers properly prepared for paper ranging from facial tissue to glassine. The volumetric capacity of a Stock-Maker is approximately 150 tons per day at normal consistencies. The put-through volume depends, however, on the type of fiber to be beaten and the amount of treatment to be given. For instance, one Stock-Maker operating at 150 hp. will treat unbleached kraft with a starting freeness of 13.5 Schopper Riegler to a final freeness of 35 at a rate of about 12 tons per day. The same machine, on glassine, will treat between 3 and 5 tons of pulp per day. The machine is usually recommended to be operated at 900 r.p.m. This speed has been found to be most economical in producing properly-treated fibers on a production basis, although other speeds can be used.

The greater freeness, usually observed by those using a Stock-Maker, means increased machine-operating speeds in many cases. The minimum inlet pressure is 25 p.s.i. As far as the actual treatment upon the fibers is concerned, the bar zone of the machine is not unsimilar to a high-grade beater. The rotor itself has integrally cast bars with very deep cell spaces between them. This element is similar to a beater roll. The shell has bars with rather shallow cell spaces, similar to bed plates in a beater. In fact, this portion of the machine can readily be considered to be a beater in which the roll has been made relatively small and the bed plates wrapped up in a circle around the roll. The portion of the machine which is unusual is the pressure and impact cycle which occurs in the inlet rotor slots and casing area prior to the fibers being submitted to the bar action in the shell area of the machine.

Practical operating experience has indicated, notably in the more free stock on the wire, that the work done on the fiber is different from other equipment.

The use of the Curlator for the refining of pulp was described by Warren A. Chilson, Curlator Corporation, Rochester, N. Y., who stated that while curlation in pulp is not new, few mills realized its possibilities until recently. A permanent change in the shape of pulp fibers is obtained by causing nodules of high consistency pulp to roll in changing directions between two surfaces which compress the nodules while they roll. As a result of this mechanical action the fibers possess more bends, kinks and twists and a more tubular cross section. At the same time a powerful deshiving action is exerted. Curlated pulp possesses higher stretch, gives a greater drainage rate, increases porosity, reduces burst, but increases tear and softness. The process widens the range of quality obtainable from a given pulp and permits entirely new combinations of pulp properties, indicating a wide variety of possible applications. It also permits a higher pulp yield for many conversions. An article on curlated pulp appeared in the January, 1950 issue of *Tappi*, pages 36–44.

The Emerson jordan control system was described by Bruno Prevost, Emerson Manufacturing Company, Law-

rence, Mass., who stated that a control system has been developed for automatically maintaining a constant pressure between the plug and the shell knives of a jordan. This control system compensates for pressure variations due to changes in incoming stock consistency, wear in jordan fillings, minor thrust-bearing misalignment, variations in stock pressure, etc. This is accomplished by the installation of a force measuring element between the thrust bearing of the jordan and an air motor. The jordan handwheel and screw are replaced with a suitable arrangement for the air motor to handle the movement of the plug either toward or away from the shell knives, regardless of rotation. Air pressure of 75–100 pounds is necessary for operation together with facilities for drying and cleaning the air.

The system is designed so that the jordan plug backs off should the jordan motor or stock pump motor stop, thus preventing glazing of the knives or tearing of the filling.

With such a control the operator can maintain constant pressure between the plug and the shell knives of the jordan without numerous manual adjustments, and as a result can have uniform stock coming from the jordan. At the same time savings can be realized through longer filling life and a reduction in horsepower consumption.

Following a discussion of the various refiners, Dr. Gallay remarked that pulp and paper makers have potentials in pulp that they do not realize. He added that his remarks of the previous day were aimed at the equipment manufacturers in the hope that they would view the subject more objectively and apply the necessary engineering to realize these potentials.

A vote of thanks was tended N. I. Bearse, chairman of the technical program committee, for the arrangement of the program and the securing of the speakers. A clambake was served on the shore Saturday noon, and Saturday afternoon was devoted to various sports. The meeting was concluded by an informal dinner Saturday evening and the awarding of the sports prizes.

Empire State

The annual meeting of the Empire State Section of TAPPI was held at the Thousand Islands Club at Alexandria Bay, New York, June 25-37, 1950. During the year the various groups, Western, Northern, Central, Eastern, and Metropolitan, have their own separate meetings, but at least once a year there is a section meeting at which the officers for the coming year are announced and affairs affecting the section as a whole are considered. At this meeting the results of the ballot for election of officers for 1950–1951 were presented: *Chairman*, Henry J. Perry, Editor, Paper Trade Journal, New York, N. Y.; *Chairman-elect*, Joseph S. Reichert, E. I. duPont de Nemours & Co., Inc., Niagara Falls, N. Y.; *Secretary-Treasurer*, Ralph N. Prince, American Cyanamid Co., Hastings-on-Hudson, N. Y.; *Representatives*, Homer M. Rice, E. I. du Pont de Nemours & Co., Inc., Watertown, N. Y., and J. F. Butterworth, Socony-Vacuum Oil Co., New York, N. Y. These individuals together with the chairmen of the various groups constitute the Empire Section Executive Committee.

About 250 members and guests attended, the program starting Sunday, June 25, with registration and an informal get-together in the evening.

Monday morning, the technical program was opened by Horace Spencer of Knowlton Bros., Watertown, N. Y. William H. Heilig of the Powell Valve Co., in his paper "Resistant Alloys as Applied to Flow Control in the Pulp and Paper Industry," briefly described the metallurgical characteristics and applications where alloys would be of benefit in pulp and paper operations. He was followed by James T. Coghill of the Curlator. Mr. Coghill outlined the developments which have occurred since this new equipment was first announced at the meetings early in 1949. Wider application of the unit is expected as well as improvement in design. In "The Practical Art of Color Matching Paper" E. I. Stearns and F. O. Sundstrom of the Calco Division of the American Cyanamid Co., Bound Brook, N. J., the third paper on the morning program, outlined in a simple manner the fundamentals of dye selection. With charts and sample illustrations they showed why dyes have their limitations and some are not suitable for use in combination to match a certain color although they appear to be of the proper shade. The final paper, by J. F. Butterworth and W. A. Beeman of the Socony-Vacuum Oil Co., summarized the various uses of petroleum products as direct additives, such as wetting agents and defoamers in the pulp and paper processes, and as converter items such as the various types of wax.

The technical program was continued Tuesday morning with Chace Mather of Carthage Paper Makers Inc., Carthage, N. Y., as chairman. C. G. Landes of the Stamford Laboratory of the American Cyanamid Co. gave an outline of the resin bonding of paper. This paper was presented at the Fundamental Research Conference which was held May 29–30 in Quebec and it is expected that it will be published in the September issue of *Tappi*. "A Review of Silicate of Soda in Paper Mill Uses" was next presented by Robert MacGonagle of the Philadelphia Quartz Co. Their use in sizing, coating, deinking, rag cooking, bleaching, and water treatment was summarized. The final paper of the technical Program was presented by George Clink of the Sandy Hill Iron & Brass Works, "Application of the OCO Water System to Paper Mill White Water Recovery." This paper was prepared by George C. Eheman, L. K. Burnett, and John C. Waddell of the Ohio Boxboard Co., Rittman, Ohio. The system described provides for the filtration and return of solids to the paper mill system.

It is expected that most if not all of these papers will appear in one of the coming issues of *Tappi*.

The social program was well taken up with golf, swimming, skeet, excursion trips among the islands, and with bridge and canasta for the ladies who attended.

Monday afternoon, the entire group was the guest of Mr. and Mrs. Abe Cooper of the Bagley & Sewall Co., Watertown, N. Y., at their estate on Cherry Island. A Frontier Party was arranged which was enjoyed by everyone. It featured a western beef barbecue.

The final affair was the banquet and annual meeting which was held Tuesday night. With Homer Rice officiating, various prizes were distributed to those who excelled in the various sports or who were lucky enough to hold the right number. In recognition of their services over the past year Earl Foster, retiring chairman, and Ralph Prince, secretary-treasurer, were presented gifts.

Left to right: R. T. Bingham, R. N. Prince, J. P. Heuer, J. F. Butterworth, R. W. Kumler, H. J. Perry, F. G. Sommerville, C. E. Foster, P. D. Switzer, C. N. Hagar, H. M. Rice, and T. E. English.

Mr. and Mrs. Abe Cooper, host and hostess at the Frontier Party which was held on Cherry Island in the Thousand Islands

After the announcement of the election of officers and a report of the secretary-treasurer, a motion was made to reinstate the Junior Award. This is made to the young man who prepares and presents an original paper on some phase of pulp or papermaking. It is restricted to persons who have not presented any prior paper and is intended to stimulate the interest of the newcomers to the industry.

The meeting was closed by the new chairman, Henry Perry. In his remarks, Mr. Perry, stated that it was the desire of the Executive Committee that all the groups would be active during the coming year, and he proposed that each group should devote at least one meeting to a discussion of political and economic events that are having an effect on the prosperity of the paper industry. He stressed that each had a civic duty and that the welfare of the various individuals and communities was each one's responsibility.

The Arrangements Committee was headed by Homer M. Rice of the duPont Co. and P. D. Switzer of the Calco Division of the American Cyanamid Co. They were ably assisted by a group which included John H. Treadwell, Earle Osterheldt, Richard Martin, Fred Ramage, J. H. Heuer, and the chairmen of the technical sessions, Horace Spencer and Chace Mather. To provide for the ladies, Mrs. Fred Ramage, Mrs. R. W. Hynes, Mrs. B. H. Cancell, and Mrs. J. H. Heuer kindly assisted the committee chairmen.

Hudson River Valley District

The following is a delayed report of the meeting of the Hudson River Valley District at the Village Inn, South Glens Falls, N. Y. on March 16, 1950. Prior to the dinner meeting, the group visited the plants of the Imperial Paper & Color Corp. at Glens Falls, and the Sandy Hill Iron & Brass Works at Hudson Falls.

Following the dinner, Harold Sholl of the Minneapolis-Honeywell Regulator Co. gave a talk on "Instrumentation in Paper Mills." This talk consisted of an explanation of a number of lantern slides showing various instrument applications.

The following is a condensed record of the discussion that followed the speaker's talk:

Question: You have recorders for liquid level. You said that they could be used as controllers. Can they control such a large stream as is sent from a fan pump to the head box?

Answer: They are used for that. The biggest problem is the valve characteristics.

Question: How large a stream can they control in g.p.m.?

Answer: I do not know, but one valve I remember is controlling a 12-in. pipe line. How many gallons per day, or per minute I do not know. You can probably better estimate the flow through the 12-in. line than I can.

Question: In regard to the Moist-o-Graph you say that it is usable in some applications. Has it been successfully used in lightweight crepe tissue sheets?

Answer: Yes. Sweet Brothers Paper Mfg. Co. in Phoenix, N. Y. has used it for that. It is the lightest sheet I know of which is crepe, and is using the Moist-o-Graph. The instrument is being used on a number of installations for condenser tissue which does not include the crepeing problem.

Question: The instrument appears to measure only a definite strip. Can it be used to measure moisture across the entire width of the sheet?

Answer: That is right. The moisture is measured only under the detector roll which contacts the sheet. Switching methods are normally included so that the operator can switch to various rolls across the sheet. Three of these detector rolls are recommended for papermaking machines and are normally enough to allow the operator to follow a wet streak and determine its location. On fast, wide machines five detector rolls might be required. Three is the largest number that I can remember on modern machines.

Question: Does that involve a multipoint recorder or a switching arrangement?

Answer: It is most advisable to use a switching arrangement. A multirecord recorder can be used, but where this is desired we normally recommend that they use a single record instrument with switching as a start. Afterward, if desired, the instrument can be converted to a multirecord type. In every case where this has been done the customer has de-

Group at the Frontier Party: Front row, l. to r.: G. E. Osterheldt, Bruce Otis, H. S. Spencer, Mrs. Fred Ramage, Fred Ramage, R. T. Bingham. Second row, l. to r. J. H. Treadwell, Mrs. Berton Cancell, Mrs. Earle Foster, H. M. Rice, Richard Martin, Mrs. J. Heuer. Rear row, l. to r.: Kenneth Carter, J. H. Heuer, T. E. English, Mrs. Homer M. Rice, and Chace Mather

cided that a single record is better. From our previous experience we feel that the single record instrument with a multiswitching device is the more profitable.

Question: At how high a consistency would you say the bubbler-type liquid level instrument would work in bleach tower?

Answer: Much depends on the bleach tower and other variables that would be investigated at the time of application. It is working to a limited extent on 20% consistency, but there are other locations where it would not give satisfactory results.

Question: It doesn't seem possible that it would work at that per cent.

Answer: Ordinarily this system can be recommended for 12% consistency with expectation that it will work. There are some applications that are working about 50% of the time at 20% consistency. There are a few operating well 100% of the time, and others have proved unsatisfactory. The unknown variables make this liquid level application a tricky job. Experience has proved that we cannot anticipate all of the variables and definitely state whether it will or will not work well at 20% consistency.

Question: Does it make a difference what material is put in them—groundwood or sulphite?

Answer: Perhaps it does, but there are examples where some have given satisfaction at 20% while others on a stock which seemed identical, have been unsatisfactory. There are cases where an 18% stock gives satisfactory operation for a few days, and then for a few days is very unreliable. On the basis of findings with these high-density stocks, their application should be considered on the basis that this instrument will operate and give better results than none at all. Perhaps you folks have some better answers.

Question: In one installation a bubbling-type liquid level worked well up to 12%, but would not give results past that density.

Answer: A similar application on lime mud at perhaps 43–45% total solids, is also difficult and frequently requires considerable application knowledge before it is successful. The air purge or bubbling-type liquid level system for open vessels have been most successful with us. There are other systems which are recommended for special applications in accord with knowledge gained through some of our failures. Frequently one instrument company does not have all the components necessary to solve all liquid-level problems. Therefore it is possible that a supplier will recommend that some particular primary device or accessory be used in order to give satisfactory operation with their equipment.

Question: Think I know what you mean—have had that experience myself.

Answer: There are any number of primary devices used to measure level. Some are of the differential type which are used on pressure vessels, sometimes for liquid level in a blow tank where the consistency may run from 16–18%. However, it is safe to say that for an open tank if the air purge or pressure type of liquid level does not work well, then the differential type as a substitution will not improve the results.

Question: How big a bubbler do you put in? Does that make any difference?

Answer: The size of bubbler pipe, or unit, recommended varies with the application. In some cases they should be quite small, in others they must be rugged enough to withstand external forces such as might be given by an agitator. The size of the bubbler does make a difference and should be discussed at the time the application is being considered.

Question: With high consistency does air come to the top of the slurry?

Answer: Not necessarily. If the hydraulic head is representative of the level, the bubble will probably work its way to the top of the material. There is a possibility that air may be trapped in the material or may be able to escape to the atmosphere without the resistance of the hydraulic head. The inaccuracies of the bubbling system are caused by the escape of air to the atmosphere without the resistance of a hydraulic head which represents level. It is possible to imagine a condition where a channel exists from the bubbling pipe to the top of the material, in which case the instrument would read zero level regardless of how much material is in the container.

Empire State Section at the Frontier Party and Barbecue.

C. G. Landes, Chace Mather, and Robert MacGonagle

Question: Does the bubble necessarily come to the top?

Answer: No. Actually if you could form a bubble on the end of the sampling pipe and hold it there, it would be a most effective way to measure the liquid level. There is a device on the market which is sometimes called "Forced Diaphragm" which is balanced on one side by an air pressure against the hydraulic head on the material side. This is very effective when the air bubbles will cause foam or otherwise contaminate the material whose level is being measured. However, the diaphragm type of primary element for liquid-level measurement ordinarily will not work if the air purge or bubbling type will not since a hydraulic head representative of the liquid level must be present. There are examples of applications which have been unsuccessful with the diaphragm unit and have worked well with an air bubbling system.

Question: Does the bubble need escape?

Answer: It can be stirred into the material, which might be of such a nature that it is absorbed. Although I have used the word air pressure, bubbling, and air purge all through this discussion, some applications have used a water purge. Just remember that we measure the hydraulic head whether we use a column of water to detect the hydraulic head or whether we use air pressure to balance the same head. Our forced diaphragm type, which most of you know about, is very useful where air bubbling can cause foaming, or other contamination in the material. An example of this contamination occurs when attempts are made to measure liquid level in sulphite cooking liquor. Air bubbles through this material will cause the formation of a glasslike material on the bottom of the bubbling pipe, and after a little time it builds up so that instead of having a sampling pipe in the liquid for 10 inches, it may be 11 inches long. This would create an error of 1 inch in whatever level was recorded, and eventually the bubbling pipe would probably stop up. Carbon dioxide and other inert gases are also used and may be desirable where air would create some difficulty in the process. There is another system which uses a filled pressure system where a completely-filled measuring system on one side of a diaphragm balances a hydraulic head on the other. This is still in effect a pressure gage and although it does not use any purging medium, the liquid-level measuring effects are the same. Regardless of the known systems used, all have the same problem, the lack of a representative hydraulic head, when attempts are made to measure liquid level of the high-density material.

Question: Is there any instrument for measuring the amount of air in stock?

Answer: There might be. I would guess you might use an infrared spectrometer. Incidentally, spectrometers have been used in the paper industry to measure concentration of chlorine dioxide in water to the third decimal place. The application was worked out by a mill who would rather not talk about it.

Question: Have you heard of any instrument to measure tension in the felt?

Answer: You are familiar with the strain-gage type of application. Strain gages can be used to measure force in a steel rod. They can be used for an extremely small or large amount of force. One application was to measure the weight of chips and liquor added to a digester. The instrument can be set at zero for an empty digester and then records how many tons of chips and liquor are added. Instruments are available with multiscale ranges so that for a full range of 5000 pounds the instrument would have five overlapping scales. The first would be 0–1100 pounds, the second 1000–2100, and the last, 4000–5100 pounds. This permits the use of these instruments for high accuracy for large forces.

Question: What kind of an instrument is that?

Answer: It uses the electronic instrument which picks up the change in resistance of the strain gage. The strain gage would be connected into a Wheatstone bridge circuit which measures the change of resistance with strain on the material to which the strain gage is applied.

Question: Can the tension of a felt be measured while the felt is in use?

Answer: In the felt, itself, no. Yes, if the strain gage is mounted on the device that puts tension in the felt. Of course, measuring the tension in the applying device is not the same as measuring the tension in the felt, but it can be a useful measurement. A common application of these strain gages is in a unit that fits onto the hook of a crane so that it weighs the load picked up by the crane hook.

An idea of how small they are made is an example of these units applied to a pressure gage. A standard pressure gage unit calibrated 0–1 inch of water could have a strain gage applied to it in order to record and transmit, if necessary, long distances the change of pressure occurring on the pressure gage element.

Mr. Hagar: The floor is open to general discussion on experience with instruments.

Mr. Hagar: Referring to one type of instrument, the measurement of SO_2 in sulphur burners. I have been fortunate enough to visit several sulphite mills at one time or another and find that most of them have had at one time or another SO_2 controllers. And a great number of them said that they just could not make them work. Some of them have continued to use them. The pens have been going all over the charts. They don't use them as controllers—they just use them as recorders. And others have just discarded them and gone back to using an Orsat again. We have had the opposite experience of having very excellent control with them. At our Ogdensburg sulphite mill we regularly control SO_2 at $17^1/_2\%$ and hold at that absolutely within $^1/_2\%$ either way. The answer to that, I have come to the conclusion, falls right back to what Mr. Sholl has said, that you cannot have successful instrumentation unless you have a maintenance program. We are fortunate to have a very good maintenance man, and a very good instrument man with a couple of helpers. When we first started it we had our troubles. He found that we had to check the thing periodically and found out when it had to be checked and made it a point to check it a few days before that period. The coke in the filter tower has to be changed periodically and the result is that now he has very, very excellent results. I don't believe he changes the coke any more often than every two months. He knows when he has to change it and changes it before that and it works fine.

Question: Do you use liquid-level control in your sulphur burner?

Mr. Hagar: Yes, we do.

Question: Along with your SO_2 recorder?

Mr. Hagar: We have found that to be very important. Even before we used it, we could keep it within 1%. The reason we are running $17^1/_2$% instead of 18% is the safety factor that comes up at that time. If we ran $17^1/_2$%, we might get up to $18^1/_2$ and back to $17–16^1/_2$.

Question: Where do you take your sample for your SO_2?

Mr. Hagar: Just ahead of the primary cooling tower. The hot gas after the combustion chamber just before it goes into the cooling tower.

Question: You are not taking it from your combustion chamber?

Mr. Hagar: No. On that liquid-level proposition—I might get in a lot of disagreement with other people but that's what we are here for—we had the type of liquid-level instrument, the bubbler type, and had the tapered plug right in the burner itself. The result of having had that plug in the burner was that quite a bit of your sulphur sprayed out into the burner. And that spray plus back pressure that you might get on your fan, your overgas, and what have you, resulted in uneven amount of SO_2. To correct that we have taken the plug completely out and have placed a tapered rod down into the sulphur melting tank. We have a small chamber on the side of the tank with the outlet raised 4 or 5 inches from the bottom so that the sediment won't interfere with it. The tapered rod is controlled from the floor above with a diaphragm valve and the results of that change in control is that we got a solid stream of sulphur-drops in, as a stream and immediately we get better results in our gas. We can run it up to $18–18^1/_2$% if we want to. That turned out to be one of the most important things—a good control of the sulphur level.

Question: With what kind of an instrument do you check it?

Mr. Hagar: We check it with the Orsat.

Question: We have been thinking of checking our instrument with gas already prepared—bottled gas 50% SO_2 and nitrogen.

Mr. Sholl: There are times when an SO_2 recorder of certain kinds—the thermoconductivity type for instance—may be affected by a trace of hydrogen coming into your sample from the moisture added to the burner in the air. Under a balanced condition a small amount of hydrogen present in the sample from the burner would cause this type of SO_2 recorder to record low. However, it might be sufficiently in error to cause any great upset in the operation of the equipment. It is well to consider that the sampling instrument may be affected by gases present in the burner which might not be present in the prepared sample. However, most instrument companies use a prepared sample as a means for checking SO_2 meters in their factories.

Question: Has anyone done metering of $3^1/_2$ to 4% stock through a flow meter?

Mr. Hagar: That can be a good question. There are a number of them on the market today. What mills have had any successful experience with them? Mr. Sholl, if the floor cannot answer, you take over.

Mr. Sholl: Stock is being measured at fairly high consistencies. Four is the highest I have seen. Venturi tubes are normally necessary if we use the conventional flow meter. Do we have anyone here from Fischer-Porter? Well, I will have to answer for them. Particularly in Canada Fischer-Porter have done quite a bit of work using a special fitting that they make in the form of a pipe tee. In it they have a formed tube and essentially a rotor so that it is similar to the common rotameter. The rotor rises and falls as the flow changes as you see it in a rotameter, and it is transmitted to a recording device. The transmission may be by electrical or pneumatic means to the recording and controlling instrument. This has been used to ratio 70% groundwood with 30% sulphite. To mention one place, they have used it at the Anglo-Canadian Paper Company near Quebec. However, conventional flow meters are being used to meter stock in two ways: one the venturi tube where the material is under pressure, and the other the Parshall Flume for stock flowing through a channel. Practical results are being obtained by both methods. The venturi tubes used are not the same construction as those used for water, and therefore should be specified for use with the stock required.

W. A. Beeman, J. F. Butterworth, Horace Spencer, E. I. Stearns, F. O. Sundstrom, and J. T. Coghill speakers at the Empire State meeting at the Thousand Islands Club

Question: What is the effect of consistency change on the accuracy of meters?

Mr. Sholl: The accuracy change with consistency is not known. The effect of viscosity change on the Reynolds number, will probably affect the accuracy of flow meters used to measure stock. However, within the accuracies required by paper mills, differential meters using venturi tubes or Parshall Flumes as primary devices have been satisfactory.

Question: Is there compensation for consistency change?

Mr. Hagar: I don't know personally but in the Fischer-Porter literature, they put out, it says that it is compensating for consistency.

Question: Will not a stock meter such as a stuff box control volume nearly as well as a rotameter?

Mr. Sholl: I would think that a stock meter of stuff box could measure stock as well as a rotameter.

Question: I was wondering myself just how accurate thel stuff box was as compared with the rotameter. I would be interested to know if anybody else has any ideas on that. We did have some rotameters in operation. We took all paddles out and found that operation was quite a bit improved.

Mr. Sholl: Ordinarily I think rotameters are more accurate than stuff boxes, but stock and other materials such as lime mud are being measured in open systems satisfactorily.

Question: On a rotameter what is the best unit or controlling variables speed. We had a lot of trouble when we used a Reeves Drive. It would grind every now and then. The races scored in the drive element and this was our principle reason for changing. We changed the drive and got away from expensive equipment and power failure.

Mr. Sholl: Would a valve do the job better?

Question: We've experimented with globe valves and diaphragm valves and they tend to plug up.

Mr. Sholl: I would suggest a butterfly valve.

Question: The butterfly valve was standard equipment before we went to rotameter to do away with it.

Mr. Sholl: There are a number of places using butterfly valves for applications never before considered possible. Butterfly valves can be used as pressure-reducing systems, one is on a 150 p.s.i. steam line coming into a machine room where the butterfly valve is controlling the pressure at 50 p.s.i. on the downstream side. They are being used to control stock in one plant at 5% consistency, and at several plants they are being used for 3½%, and are doing an excellent job. Hills-McKenna or Saunders type valves have been used in a number of places. Some applications are using Crane Bonnetless Gate Valves. However, the throttling characteristics of a butterfly valve properly sized gives perhaps the best results.

Mr. McCourt: I would like to add a little to the Fischer-Porter Rotameter discussion. We have one in our bleaching operation and controlling our chlorine in our chlorination stage from a Ratosleeve. I will say it is pretty successful. Not too sure we have all the kinks ironed out of it. As far as the Ratosleeve is concerned, I think it is pretty accurate. It does give a method of controlling our chlorine addition with changes in stock flow.

Mr. Hagar: Any other questions from the floor. I would like to get some of you fellows in on these answers. We all have questions; we all have answers. So far we have asked the questions. Very few answers from the floor. Mr. Sholl has had to do all the work for us.

Question: Application of liquid-level gage—when air goes off on the week end the pipe line plugs up. What can be done about it?

Question: What's the cross section of your pipe?

Answer: About ⅜-inch pipe.

Question: Ever try 1½-inch pipe—to go through your clay slurry?

Question: A 1½-inch pipe to go to your bubbler?

Answer: You won't plug up a 1½-inch pipe as fast as you will ⅜ inches in diameter.

Answer: The air comes through a ⅜-inch pipe.

Answer: The cross section of the pipe has no bearing on your sensitivity.

Question: With regard to that question, what would you do about the plugging of the bubble-type liquid-level system? You will have less trouble with a large pipe. I have seen them up to 2 inches. As they small down they react as if the liquid level is changing—as if you had more displacement to account for. They do not affect accuracy at all as far as level is concerned.

Answer: In regard to washing the line, we have a water line hooked in so that if the air goes off, water automatically washes the stock out of there. It is built right into the arrangement.

Answer: There is nothing peculiar to that. We have done that same thing. It is just putting a valve in the line.

Mr. Hagar: I know one of the things people have run into in digester control has been liquid level. We at Ogdensburg have a control system on the cooking and have liquid-level differential type meter with automatic purge. I forget now what the size tubing was in it. We had quite a bit of trouble with it. The darned thing was always plugging up. It tended to plug up at the point of entry into the digester. Spent some little time with ideas in trying to get air out of the water. We thought that it might be the air, and it undoubtedly was the air on the intermittant automatic purge that was plugging up the end of one tube. It caused quite a bit of trouble. Finally the problem was solved by putting a larger tube in than we previously had and secondly—again I might have an argument very easily—the automatic purge did not seem to work well. The system was changed over to manual purge. It was set up to purge once or twice a shift. They just completely flush out their line and at the same time they release air that might have built up in their manometer setup. It has worked fine ever since. I understand that a few mills have had trouble in that application.

Mr. McCourt: There is one type of instrumentation we fooled around awhile on and finally gave up. That was to measure chlorine with a rotameter. I understand that this is successful in some places but we certainly could not get it to work. Ended up by weighing the gas.

Mr. Hagar: I have seen that in operation—I think out at Northwest in their new bleach plant. The only thing I understand they have trouble with is that they get a certain amount of oil with the gas which tends to contaminate their rotameter so that you could not see the thing and you have to take it out every once in a while. That was a couple years ago. Don't know what success they have had since.

Mr. Moynihan: How much difference would that be, Mac, in SO_2 or chlorine? We put SO_2 through.

Mr. McCourt: Get the liquid?

Mr. Moynihan: Yes.

Mr. McCourt: I don't know. Ours would not work at all—whether it was us or the instrument.

Answer: They say it is the air that causes the trouble. You have excess pressure that holds air in solution.

Mr. Moynihan: We might have had more gas pressure than water pressure. That might be the answer. The water pressure drops and the gas pressure is too much. It just won't work.

Mr. Hager: Also, perhaps the location of the needle valve after it might have a lot to do with it. We put one of the systems in just a short time ago knowing Bob had had good success with it and we have had very little trouble in that respect. I believe that you folks once said, Bob, that if you have too much head between the tank and the rotameter, you get into trouble because of your pressure on the tank.

Mr. Moynihan: You have to have more air pressure coming through. When the air pressure gets below actual tank pressure, then you get into trouble.

Mr. Hager: We have exceptionally good luck with SO_2 and I guess we have 15–20 feet rise from tank to rotameter.

Answer: On the bubble-type liquid-level gage, we control the amount of air in pipe by using orifice and we have found that we use no more air using larger pipe.

Mr. Hagar: There are a lot of people interested in paper machines in this neck of the woods. One thing we have found—to continue talking about our own experience—a year or so ago the question came up as to whether you would need an outside air pipe for measuring headbox level—there is the possibility of air entrainment and we thought about that for a while and planned to drill into one headbox and put a standpipe and bubble tube arrangement in that. We thought, we will try it without it at first and then if we are in trouble, we will put a simple bubbler tube over and down into the headbox. To date we have them on many of our machines. We do not have a bit of trouble with it. It is a very simple application. We have large volumes of water going through. We have gotten fairly sensitive instruments in the 15 to 25-inch range and where you are changing your speed very frequently we have taken interchangeable tubes and shown on the headbox what each tube will correspond to in speed, etc. For anybody interested in that thing in open-type headbox you can just put a bubble type in and you have a perfect place for instrumentation.

Question: Does stock build up on the sides and break away?

Mr. Hager: No, we have not had that trouble at all. There is perhaps enough turbulence in headbox that prevents that.

Question: How far back do you put pipe?

Mr. Hagar: About any place, we have moved it around. We have one just behind slice. It is a very high headbox. Have had it in the back and sides and in no case has there been any entrainment. When the mill first thought about it,

they put a standpipe down into the headbox, to still it supposedly. They did have trouble. The stock did collect all up and around the standpipe, broke off, and gave trouble. Now we have 3/8-inch copper tubing and have no trouble at all. Lot simpler than we thought it to be.

Question: That a recorder or indicator?

Mr. Hagar: That is a recorder. We have liquid-level recorders. Cost from $100 to $150 roughly, and very simple to put in.

Floor: Just a little experience that might be of interest to the men. You are perhaps saved in your case by the range of the instrument you mentioned. If you are amplifying the liquid-level movement on, let's say, an instrument chart where the liquid level may be moving an inch, you are actually moving the pen 2 inches. You will find, I believe, that if you do not take some precaution to still the hydraulic head adjacent to the bubbler pipe, you will get an effect on the record that is not satisfactory. So you can put a stilling tube in, that gave you trouble, but if it is looked after and correctly designed it will give very satisfactory records. Without it, if you amplify the movement too much, you get pretty ragged records.

Mr. Hagar: Do you think you ever need to amplify your movement much more than to show an inch or 1/2 inch or the sort? If you have to show a fraction of an inch, and you might have to in some cases, then maybe you have something. Normally an inch of head will tell you quite a bit.

Floor: The application that I refer to was made at the request of the papermaker. Do not know whether or not it is necessary to hold the head within such close limits or not. He thought it was. Such records we could get with a normal pressure instrument were not satisfactory. It had to be amplified. It wasn't satisfactory until we supplied the stilling tube around the bubble pipe. To just give a rough variation on that, we found the one inch of head on the speed of the machine in which we use these instruments—one inch of head makes a difference of approximately 7 to 9 f.p.m. So actually if you are varying 1/2 inch on your chart, you vary from 3 1/2 to 4 1/2 at the very most, feet per minute. You aren't controlling your machine much closer than that so we feel we are within safe limits under the conditions that exist.

Mr. Hagar: That has been a simple application we are very pleased with. It saves the machine operator from always running up and down stairs to look at his level. Think it is well worth that to him. When you first put them in you start to have trouble with things you haven't anticipated. Before we put them in they did not think they would be any good at all. After we had them in they were chasing after us every 5 minutes if anything went wrong. Saves steps, and people appreciate that. And also it is one time when that type of instrument really paid off. We found as I suppose many of you have found that papermakers all have their own ideas. A man would come on shift and he would immediately change 5 or 6 things including the head and he would fool around with that all shift and when the next man would come on he would change everything again. The paper mill superintendent did not think that was the thing to do but had no way of proving it until these recorders were put in. Now he can see just exactly what has happened and we have kept the things down to a great extent. If any changes are made, they are right there. The men hesitate to make them now without thinking three times about it.

There are some logical places where instrumentation can really pay off. How about some other ideas.

Floor: In our plant we built a head gate about 1/3 miles from the generator room. It was very beneficial for the operator to know how much water was behind the head gate. We installed a stilling pipe beyond the headgate and a diaphragm in the raceway with copper tube to the generator room and recorder where our generator operator can have a record of water above the headgate. It works swell.

Floor: You need never worry about ice in the type liquid-level gage you have mentioned if in your weir box or in your stilling well you put a 100 watt light bulb. I know of three installations upon the Oswego River where they run 25 to 30° below zero—just a 100 watt light bulb burning down there.

Question: How do venturi for stock and water differ?

Mr. Sholl: Guess I was the one that mentioned that. Venturies are different for stock and for water. There are quite a number of things that are different. One is the way in taking the throat pressure. The casting is made differently. The other is in the degree of finish. A smooth venturi on stock does not give consistent results. Why? I don't know. There is some theory about it by the people who supply pumps and bigger piping that stock flows better in a rough pipe than it does in a smooth one.

Question: Do they smooth the inside of the tube?

Mr. Sholl: The venturi does not have a smooth finish, it is not polished. The Simplex Meter Company and Bilder's Iron Foundry has had considerable experience in these units and furnish the venturi tubes as required. Perhaps a different Reynolds number is used or their calculations are slightly different.

Question: Is the upstream tap still one pipe diameter?

Mr. Sholl: I think the answer is yes. Others may be used where a necessity demands or the mill specifies. The downstream tap, which in this case is the throat tap, is very critical.

Question: At what consistency do you change over from a water to a stock orifice?

Mr. Sholl: Our experience is to use an orifice plate for most applications where consistencies are at 1% or thereabouts. Where consistencies are around 3 or 4% a venturi or flow nozzle is recommended. Decision as to which should be used is either left to the mill preference or the approval of the flow calculation engineers in the factory whose experience indicates which would be the more successful.

Mr. Hagar: Has anybody found any advantage in temperature control in your circulating water on paper machines, your wire pit, headbox, etc? Anybody had any particular experience? Obviously, it is very worth while in the control of temperature in your paper machine headbox. Any interesting application; anything that would justify such a system being put in.

Question: Is there any particular temperature you would like to hold on it?

Mr. Hagar: I am asking a question. If you have a change in temperature of your water, theoretically at least, it will make a big difference in your drying and as a matter of fact, it is something you will find in any instrument company's booklets on paper machines and I have just been wondering about any actual applications.

Floor: Years ago we put that in for the advantage we got on startup. We actually had to steam it then some. We added it until our recorder indicated some temperature, then we were ready to start up. We also held. In the wintertime we closed our system to hold our temperature as desired.

Mr. Hagar: Are there any additional questions? This is a good time to get anything off your mind on instruments.

Well I think that just about winds us up tonight. Just want to add in closing a personal viewpoint that instruments are something that can do you an awful lot of good. The choice of the ones you use will depend completely on what you want to do. As has been brought out several times tonight, a simple instrument will do your job rather than a high priced one. The instrument companies are only too glad to suggest that type of application to you. But as I have said before anybody who is considering instrumentation, who may not have it, or is going to more complicated instrumentation, has to remember that it is not easy, that you can abso-

lutely ruin the application of instruments in your mill by having improper maintenance. And it cannot be one of those things where you wait until you have trouble and then go out and fix it. You have lost half the advantage of the instrument there. You have thrown your whole system off because the men will get so they rely upon it.

Meeting of April 20, 1950

The Hudson River Valley District of the Empire State Section met on April 20, 1950, at Mechanicsville, N. Y. A feature of this meeting was a visit to the mill of the West Virginia Pulp and Paper Co. Following the dinner L. M. Woodside of the Albany Felt Co., Albany, N. Y., gave a talk on "Fourdrinier Machine Felt Problems." Mr. Woodside's remarks follow:

"The paper mills included in the Hudson River Valley Section of the Technical Association are mostly fourdrinier mills and so I propose to confine my remarks mostly to felts and felt problems which are met in that type mill.

"My talks to paper mill groups in the past have been mostly in discussion of the things which can go wrong on a paper machine and which will affect the felt problem on that machine. I do not mean to intimate that felts are always perfect, nor that every felt does its job perfectly. I do claim that if a machine problem is properly analyzed, and the proper felt designed for that particular job, then our controls are good enough so the felts you receive will continue to do a good job as long as the machine conditions remain the same.

"We must do better than that, though. It is a well-known fact that a machine to be kept in its best condition must have constant attention. A program of maintenance must be used which will assure the machine being in its best condition at all times. With the newer high-speed machines, running over 1000 feet a minute, that maintenance program must be adequate. On the older slower speed machines, such care is probably not necessary as the variations in operation do not have the tremendous effect on the good operation of the machine.

"My father, who spent most of his life over at the Hudson River mill of International Paper Company, was what we hear called an 'Old Timer.' He could feel of the stock in the beaters, then in the head box, then look at the wire for a few minutes. Then he would give the hand wheel on the jordan an eighth of a turn, go back and look at the wire, and soon tell the machine tender to 'take it over,' and they would make paper for the rest of the night.

"While that type of papermaker is still in existence, and while he is invaluable to many mills, he is now being aided by automatic controls and scientific measuring devices. I do not mean to infer that we do not need men like that, but the days of the one-man paper mill are fast disappearing. There are so many scientific and mechanical aids now available, that the importance of the 'Old Timer' is becoming less and less. By use of the scientific developments we are getting down to the fundamentals of papermaking.

"It has been my experience that in the paper industry and felt industry, there are certain fundamentals which can be established and which will make all our jobs easier when they are recognized. The felt industry is behind the paper industry in development of these fundamentals. The time is bound to come when we can establish certain truths, and be sure that in the cases where the truths do not seem to agree with facts, that there are other contributing factors clouding the picture. Then, knowing this, it is easier to determine the exact trouble.

"I might cite two recent cases to illustrate this. One has been worked out and the other has not.

"I recently called on a mill which complained that our cylinder top felt was wearing in streaks. Knowing that our manufacturing records were normal and further, knowing that two of six felts made at the same time had been all right, it was almost certain that something had gone wrong on the machine. In a series of several felts woven at the same time, the same warp yarns extend through all of the felts, so it is unlikely that there would be that difference in behavior. It was noticed that the top felt was stretched on the back side so it was slighly baggy. It was also noted that the new bottom felt was very slack on the front side. Knowing that there must be something on the machine to cause these felts to run as they were, we started making measurements of felt stretch and roll speeds. It was found that one of the press rolls had had the journal broken recently and they had patched it up in order to run the machine until a new journal and coupling could be purchased. This bottom press roll was badly out of line, and, when it is corrected, I am sure the felt life will return to normal.

"In the other case, we had a mill using a certain type of pickup felt on high-speed tissue. They ran into some trouble and we recommended a change to a felt which not only should have overcome the trouble but which should have been a better type of felt to use for all-around operation on that machine. One of these felts has been run and the mill had trouble which they should not have had with it. In every other case this change was an improvement so, in this case, there must be other factors affecting the operation of the felt. If we can find those other factors, we will be able to correct the condition. We know the fundamentals of pickup felt operation and can therefore look for other factors affecting the operation of that machine.

"Now, if we can establish the fundamentals of felt operation for all types of felts and all types of paper, we will be able to do a better job for you as papermakers.

"Getting back to fourdrinier felt, it might be well to discuss the type of felts, and the different weaves used in these felts, to give you a better knowledge of what you are working with.

"There are two general classifications of fourdrinier felts. The 'wet felt' and the 'press felt.' Under the first we have the common wet, fine wet, superfine wet, and the extra superfine wet felt. Under press felts we have the fine press, the superfine press, the plate press and the super plate press. Each step up to another group is to a finer felt.

"A fine press felt, however, is not necessarily finer than a fine wet felt. We might roughly say that a fine press felt is similar in fineness to a common wet, a superfine press comparable to a fine wet felt and so on. The difference between the different groups of wet felts is determined by grade of wool, size of yarn, number of threads or yarns per inch. The standards reflect in general the cost of manufacture.

"As to weaves, there are five basic weaves used in the felt industry. I have woven pieces of cloth using cotton warp yarns and blue woolen filling yarns which will illustrate the difference between these weaves.

"The plain weave is the oldest of the weaves. It has been used for many years. It simply has the filling yarn passing over and under one warp yarn at a time, with each row alternating. You will see from the depth of color that this makes a felt with the same amount of filling yarn on each side.

"The first step away from the plain weave in the direction of better finish was the use of what we call a broken-twill weave. In this weave, every second filling thread is woven as in a plain weave. The other filling threads pass over two warp yarns, then under two warp yarns.

"In a further effort to gain better finish and to give greater openness to a felt, the one-sided weave was developed. I would like to correct one misunderstanding at this time, many papermakers refer to a one-sided felt as a felt with more nap on one side than on the other, this is not true. A one-sided felt is a definite weave which has more filling yarn on the one side, or top side which is against the sheet, than on the other side. In weaving this felt, the filling yarn passes under one warp yarn and then over three warp yarns. In weaving a felt of this type there are just half as many crossing or knuckels of warp and filling yarns as there are in a plain weave felt.

"Since, in most cases it is the knuckles formed by the warp and filling yarns which mark a sheet of paper it is easy to see that this weave will give better finish. Since there are half as many crossings of warp and filling yarn, you can see too that the one-sided felt is more open than the plain weave. From the weave sample, comparing the plain weave with the one-sided weave you will note the difference in color when comparing first the warp side and then the filling side of these two cloths.

"The great difficulty with a one-sided felt is that unless the felt is extremely fine, it is not possible to turn the felt and get the same finish on both sides. Since it was necessary to do this and yet get the better finish of the one-sided weave, the two-faced weave was developed. This is simply a one-sided weave, doubled. The first filling yarn is woven with a normal one-sided weave, over three warp yarns and under one. The next filling yarn is woven under three warp yarns and over one. In making a two-faced felt and keeping it in the same class as a one-sided felt, the resulting felt must be coarser. For instance, a one-sided common wet felt can have 18 filling yarns per inch. To keep a two-faced felt in the common wet class, you can use only 18 filling yarns per inch or nine on each side.

"This gives us a felt with the same finish characteristics on each side and more bulk than with a plain weave felt. It does normally make a closer felt than a one-sided felt if made to give equivalent finish, and is used mostly in making press felts where bulk is needed in the felt.

"The straight-twill weave is much used in making wearing apparel. In the felt industry it is used in making pickup felts and some very fine press felts. It cannot be used in a coarser felt because of the extreme wale you will note in this weave sample. This would mark the sheet very badly. On the felts where this weave is used, the filling yarns are mostly more than 100 per inch so you can see that the wale would be so fine that it would not be noticeable.

"In my discussion of weaves, I have given you the general

differences, assuming that comparable felts are made with the same yarns and the same yarn counts per inch. In changing from one style to another it is often necessary, for better manufacturing methods, to make some alterations in the yarn count in either the warp or filling, so the differences in the felts are not usually as simple as just a change in weave.

"Now you, as technical men, are interested in cause and effect of different changes on your paper machines. You are interested in determining the best and cheapest way to make your particular grades of paper. It is not always necessary to have a definite felt program to establish best operation, but it is always worthwhile to have records to help determine the factors which have the greatest effect on felt performance.

"Much work has been done in an effort to determine an accurate method of determining the best felt to use on any particular position. The old method, and the one in most general use today is the cost per ton of paper produced. This is not a good measure of efficiency of the machine. After all, it is the final conversion cost of paper which is the determining factor in your profit and loss statements. Felt cost per ton does not include, in most cases, the steam cost, speed, nor the rejected paper which cannot be shipped.

"Felt companies are fast approaching the point where they are selling efficiency of operation rather than felts. Those paper mills who can determine this efficiency, and, I'll admit it is hard to do in most cases, are those who are getting the best results.

"I could cite innumerable cases where more or better production has been gained at a higher felt cost, but where the over-all conversion cost has taken a decided drop per ton. I will give you one good example—in a southern mill making kraft paper the wire life was 12 days. The first felt ran about 14 days and the second felt ran about 15 days average. This mill was having 18 wet-end breaks per month. As an experiment, they decided to change their felts every time they changed the wire, or on a 12-day interval. The only immediate gain which was noted was that the wet-end breaks were reduced from 18 to 5 and even went as low as two breaks per month. These breaks averaged not over five minutes of lost production but they more than saved the cost of the felts by simple elimination of these breaks. With such a gain, this mill started plotting machine speed against the age of their felts. They found that in the two-week period one machine speed was reduced 6% by the end of the period. They are at present working with the felt companies to obtain felts, or better methods of operation, which will eliminate this reduction in speed. When the final results are attained, they will have a much more efficient mill than they have now.

"I can remember when I started working in a mill in this area, fresh out of high school. I was the fifth hand on a news machine which was being converted to specialties. They must have had some trouble with their felts as one of my duties was to tighten up the stretch roll after the felts were washed. As I remember, I spent a great deal of my time tightening that stretch roll.

"I think that filling up of felts, is probably the greatest trouble you have with an open fourdrinier machine. This is because of the heavy sizing and filler materials used on the grades run on these machines.

"There is considerable that can be done to help these conditions by changes in felt design. Assuming that the felt design is correct, however, we must find means of cleaning the felts to prevent costly shutdowns. I have seen machines which had to shut down four or five times a day for from $^1/_2$ hour to $1^1/_2$ hours to 2 hours, and these were not all color changes either.

"If a method could be developed to properly clean these felts or to keep them clean while running, it would certainly improve the machine efficiency and so lower the cost of conversion. There are several felt conditioners on the market at the present time. With the proper installation, these conditioners do a good job.

"Much can be done by proper use of suction boxes in conjunction with warm-water showers. I personally think a detergent could be developed which would clean a felt on the run when used in conjunction with a suction box and warm-water showers.

"Many people use spread rolls and wormed rolls to good advantage. It has often been said in the past that all of these methods of keeping felts clean are hard on felts. I will grant that they are hard on felts, in varying degrees, but your job is making paper and, if a wormed roll or a felt conditioner enables you to operate a felt at higher speed, or at higher efficiency, then the felt cost created by the wear of these units is much less than the gain in quality or production.

"One of the greatest factors which cause short felt life when using felt cleaning equipment, is lack of lubrication, water lubrication. For instance, if you use a suction box and a shower some place on the return travel of the felt, there is much less wear on the felt than if the suction box is used without a shower, or is used on the felt and sheet where there is not sufficient water to lubricate the suction box cover. I have seen machines with as many as three suction boxes in a row on the felt, ahead of the press. If the felt is wearing out, it is probably the third box which is doing the damage, as the felt has been dried out enough that there is not sufficient lubrication to keep the felt from wearing.

"Getting back to a felt program, there are certain things which can be done, in conjunction with the felt maker which will pay dividends to you. The object of this program must be such that you eliminate the guess work and get down to the fundamentals of felt use so as to determine whether a certain design of felt does a better job than another design. A close record should be kept of exactly what happens to the felt on a certain position. For instance you must know the grades and weights of paper run on any felt. You must know the crowns used on the rolls while the different felts were run. You must know whether any peculiar condition has developed which might have an effect on the felt performance. As an example of this I might tell you that it often happens that one of the primary presses on a board machine is removed for grinding. This increases the proportionate weighting of the other presses, and will possibly affect the results from any particular felt.

"A record should be kept as to the draw on a felt. Some felts are, as you know, run more tightly than other felts. This will not only have an effect on the felt life, it will effect the efficiency of the press and of the cleaning equipment. The tighter a felt is, the more damage will be done by your cleaning equipment. If you have felts from two makers, you should be able to tie in the weight, porosity, and method of operation of the different felts with the best practice in your mill.

"You should keep a record of how the felts wear out. If, for instance your felts are all removed because they fill up, then you can either improve your cleaning methods, or purchase a felt which will fill up less. If you realize that the felt should be worn out when its efficiency starts to drop, then you will get more out of your felt dollar. If a felt is not approaching its worn-out stage when removed, then you are wasting money, or are not cleaning felts properly.

"In my opinion a felt is like a chicken. Farmers all say that when a chicken is born there are so many eggs in her breeding. The sooner you get those eggs out and sell the bird for meat, the cheaper you are able to run your farm. With a felt, the sooner you get the eggs or dollar value out of it, and cut it off, the better off you are.

"Is it not better to keep a felt clean and wear it out three days sooner than to slow down and take the felt off because it will not make paper, after several washups?

"One of the greatest sources of trouble with felts on modern high-speed fourdriniers is that of shadow marking or suction-hole marking. I have done considerable thinking about this problem as we have been called upon many times to correct the condition. Personally, I do not believe that shadow marking is a felt maker's problem, although we are saddled with it.

"About all we, as felt makers, can do to help this condition is to make a more bulky felt. This apparently eliminates the trouble in some cases. We still have the fact though that some mills can run common wet felts on book papers or sulphite papers and not get suction hold marks, while other mills must run a super plate press which is a much more expensive felt, to even minimize the mark.

"We know that soft rolls give less trouble with this mark than do hard rolls, and we know that less-hydrated stock is less likely to mark than well-hydrated stock.

"I have been vitally interested in this problem because as with all other felt problems there must be a solution. The arguments I have heard most are whether the marked spot of the sheet is wetter or drier than the unmarked spot. There seems no method of determining this. Recently, I talked with a machine engineer, who has given me the best answer I have heard yet. He claims the mark is caused by pressure. He says that as the sheet passes through the nip of the press, the paper is depressed into the holes of the suction roll, and a mark develops. To substantiate his story he says that if the holes in the suction roll are worn, causing suction marks, they can eliminate them by grinding the roll which makes the top of the holes smaller and straighter. He claims further that by drilling rolls with smaller holes and more of them they can eliminate this trouble.

"This theory answers most of the questions, at least in my mind. It explains why softer rolls cause less mark than hard rolls. With soft rolls, the nip area is wider so there is less pressure concentrated at the point the sheet crosses the suction hole. A smaller hole will not allow the sheet to be depressed so much. A bulkier felt will create less pressure per unit area.

"His answer to the problem is to follow a suction press with a plain press, with sufficient pressure to iron out the unevenness caused by the suction press. He claims that with machines where this practice is followed, suction-hole marking is not a problem.

"It is this type of investigation, where the machine builder, feltmaker, and papermaker cooperate that we can all eliminate the difficulties which we have. In other words, if we can get down to the fundamentals, we will gradually make our jobs easier and certainly more enjoyable."

Question: Regarding nylon felts, is it not true that nylon is more subject than wool to attack by mineral acid, which leads to a point that with nylon there is a limitation to its use on machines where you have a fairly low pH by alum or acid? Say in the normal range of 4 to 5.

Answer: Our laboratory is working on that and our first report is that strong formic acid is the only one which seriously damages it. Any acid would have to have a much greater concentration than is obtained in the paper mill, to harm nylon fibers.

Question: Are there any materials other than nylon that are used?

Answer: The Lockport people have used a material known as Saran. I think they are using it in felts at the moment. I do not know too much about the results. Some have been good and some bad. We have investigated Saran, and within the last few years have investigated other new fibers that DuPont has brought out, hoping to use them in felts but nothing has come up to nylon. That is our own experience.

Question: Say anything about properly breaking in a felt?

Answer: I would like to, but I am again going to say things that some of the felt companies will not agree with. My approach to the felt-paper problem is from your standpoint. I believe that a felt should break in very quickly. Will say that on an extremely wide machine—let us say a machine of 200 inches or more—or probably the same thing is true on some narrow machines, if the felt is not wet up uniformly and broken in properly the chance of so-called dry wrinkles in the center of that felt are very possible. We have had several cases where that has happened. A brand new felt will go into a wrinkle as soon as they try to shrink it or particularly, let us say—where a mill has changed from a 150 to 240-inch machine because you cannot use the same shrinkage methods with the wide machine as you can with a narrow one. Frankly, on most machines I would say from my experience that you can slap the water to it and within 20 minutes to $^1/_2$ hour make paper, depending of course on the type of felt, type of machine, warm or cold water or several variables.

Question: Should a new felt be started flat or roped up?

Answer: I would like to say, and I believe that other felt men will agree with me, that a felt should always be wet out flat, never roped up. Because when you rope up a felt and wet it there is always a possibility that there is one streak in there that will not wet up and it won't shrink properly. Now that precaution is much more serious on a press felt which wets up slowly anyway than it is on a common wet felt which has more tension and will shrink back much more easily. We recommend that a felt be pulled out flat, that the stretch rolls be pulled out lets say two thirds of the way on the thread and that the felt be wet up uniformly. The best way to wet a felt, of course, is to put a shower on it. As the felt is wet up move the jack back as the felt shrinks. That is the safe way to wet a felt. Quite a lot of poeple do it, but there are not too many of them yet. If your machine is down, you cannot monkey with stretch rolls. I know of one mill which actually changes 3 felts, a wet felt, and two press felts in 22 or 23 minutes. It is a southern mill with dual press so that they do not have many rolls to handle, but brother that is getting on the ball.

Question: How much tension should be applied to a felt during operation?

Answer: I can say as a feltmaker that a felt should run just as slack as it can be run on your particular position. Now there are some superintendents who believe, particularly on some board machines, that a felt is made to run tight. That is not true because you can picture a board-machine felt as being similar to a rubber band. A felt is made with elasticity. As that felt is pulled out longer and longer, you reduce the elasticity. The tighter the felt the more wear you will get from slippage on your presses, from suction box covers, from whippers, from holes in cylinders, from over anything. I like to put it this way—a board-machine felt, let us say, is made 150 ft. If that felt does not exceed 150 ft., I do not give a darn if there is 6 or 7 or 8 feet of stretch in the felt, but if it goes out beyond 150 ft., then 2 ft. of stretch is too much. The same thing is true of slipping on any press. If the press is perfectly smooth, it will not have any effect on the felt, but if you have a pitted brass roll in there a tenth of one per cent can chew out of the felt. The slacker you can run the felt and make paper the better operation and the better felt life you get.

Question: From your experience with felts what limitations are there in practical papermaking, with normal things we use in papermaking in a chemical way, to give felts their maximum life? Are there chemicals or complications of which to be careful?

Answer: You hit on a pretty broad subject concerned—I am talking about cleaning and whatever goes into or onto a woolen felt. I would say that you very definitely want to keep from trisodium phosphate. Na_3PO_4 in our experience is the next thing to caustic soda. Caustic soda is probably the worst thing you can put on a woolen felt. Now, in the same line, in your normal chemicals which you use in papermaking there is little if anything that they can do in themselves to injure a felt. Calgon as far as we know does not hurt a felt at all. Alum and size in themselves do not hurt a felt but alum and size help a felt fill up and the filling up can do much more damage than the actual chemical action. Furthermore—I think it might be of general interest that we find that more of our bacteriological problems in the warm weather are in mills running from neutral up. We know that acid deters bacterial growth. We know that the mills that run a pH of 6 or lower have much less trouble with bacteria than those that run near neutral or on the alkaline side. It can be safely said that outside of Na_3PO_4 or other active alkalies, that the effect on the felt is rather from what the chemical allow to happen rather than from the direct chemical action.

Question: On what do you base the percentage of nylon fiber used in the filler?

Answer: When the first experiments were run with nylon yarn or nylon staple, we had a wear curve which I presume was made in ladies' hosiery—a wear curve showing that resistance to frictional wear was a curve that went up quite rapidly and then flattened out. We took an arbitrary percentage of 25% in the filling as that which gave the greatest gain most quickly. We started with 25% nylon in the filling. In our experience in manufacturing felts we found in some cases that this was too much, and we have made some felts with reduced percentages. The difficulty with the experimental program is that it entails so many different yarns. When you figure that a felt mill the size of ours handles two or three hundred different styles and several hundred different yarns and to get proper experience you would have to spread it over all types of felts, it would mean a tremendous job that with the rush of business for the last several years we just do not have time to do.

Question: Have you tried using nylon in warp?

Answer: Yes, we have done some work with percentages of nylon in the warp. It is probable that nylon, wisely used, will be helpful—some cases—the warp. More work remains to be done on this.

Question: Is there truth in the report that nylon threads in fill are cutting or wearing the warp threads?

Question: Well, there is a question. There is a possibility that the harder yarn caused by using nylon in the filling injures the warp on machines where they press harder than usual. Whether the filling yarn is cutting the warp yarn or not we do not know for sure. Frankly, on the physical characteristics of the two yarns it does not seem possible. That is, the filling yarn is bulky and soft and it does not seem possible that the bulky, soft yarn would cut the harder warp yarn.

Question: Did you reduce the percentage of nylon because of excessive wearing of warp threads?

Answer: That is one of the reasons we tried reduced amounts. We are not entirely sure it was the nylon causing the warp threads to fail. Our end of it is just as confused as your judgment of a felt. We have many side off-shoots to eliminate, and you know the manufacture of felt takes quite a while. But we are working at it. We hope to have an answer.

Question: What is the heaviest sheet being picked up on felts? I am referring to M. G. papers.

Answer: On a M. G. sheet the limit is not heaviness of sheet. Have seen one on 90-lb. sheet but they raise top couch roll because they didn't need a pickup felt. I think frankly, you could pick up 50 lb. but do not know how fast. As far as I know, the weight of the paper has relatively little to do with the ability of the felt to pick up.

Some years ago we started some very interesting work on pick-up felts. It cost us some money but we obtained some information nevertheless. The trouble we had heard about was trouble starting up. I went to several mills and asked them if they had trouble starting up. They said, "No." I finally arrived at a mill of a very good friend of mine, asked the same question and got the usual answer. During our talk he said, "We are putting a pickup on No. 7. Do you want to see it?" I went down there was enough hay on the floor to fill this room. So I said "What do you mean, you don't have trouble starting up." He said, "This is normal." So then when I started asking questions such as, "Do you lose any production." I found out that a lot of them did. Now, with the work that has been done in improving pickup felt design, the complaints are very, very few.

Question: Would you use a more open felt for top suction couch?

Answer: I do not think so. It does not agree with what's been done. What I would have in mind to make the machine work is not a more open felt. You see the difficulty with suction is that the suction draws fibers into the body of the felt. When you get cellulose fibers into that felt your felt is waterproof and it just won't do anything without crushing. So I maintain that an open felt will allow those fibers to collect more quickly than a pickup type of felt.

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Economies in the Magnesium Oxide Sulphite Waste Liquor Recovery Process

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RECENT papers presented by F. E. Hutton at Montreal and R. E. Baker (*1*) at Portland have covered the mechanical details of this process as well as early operation efficiencies.

In the meantime, since those papers were presented, the following three operational changes have been made which have permitted increases in capacity and have allowed for better evaluation of losses throughout the system.

While originally the multiple-effect evaporators were operated as a six-body quint, they are now being used as a six-body quad to increase evaporating rates at the required high-liquor concentrations. Provision will be made to return to quintuple-effect operation because of the steam economies possible.

Originally the concentrated red liquor from the multiple-effect evaporators was passed through the cascade evaporators for further concentration and consequent cooling of the recovery furnace gases before being fired in the recovery furnaces. However, this liquor cycle resulted in the formation of foam and of calcium sulphate scale in the cascades both of which caused frequent interruptions in the fuel supply to the recovery furnaces. To avoid these effects, the liquor cycle has been changed in order to pass the weak liquor from the washers through the cascades for initial concentration, then through the neutralizing tank to the multiple-effect evaporators. The evaporators now deliver the final concentrated liquor through the heavy-liquor storage tanks, functioning as the evaporator flash pot, to the furnaces without dilution from direct steam heaters. As a result we are able to operate the recovery furnaces continuously with liquor of elevated concentrations without interruptions from scale or foam.

This latter change in the liquor cycle further permitted us to control effectively the alkalinity of the liquor to the multiple-effect evaporators and maintain a pH of 7.0 continuously during our latest survey of system performance, thereby reducing the amounts of sulphur lost at the evaporators.

Since no major changes have been made to the system, it is our thought that at this time we should concern ourselves with present plant efficiencies and from these data attempt to arrive at performances which can be expected under conditions when known losses have been reduced to what we consider to be economic values.

In developing the possibilities inherent in this process, we have divided our presentation into two parts: first, in order to establish what is representative of present operating conditions of the Weyerhaeuser plant at Longview, we have assembled an itemized tabulation of losses. Secondly, on the basis of the above tabulation and on the basis of experience gained in the operation of the various units, we will endeavor to present a balance in which all losses have been reduced to economic levels as applicable to the present Longview installation.

During the period of March 9 through March 18 of this year, we conducted an intensive survey covering the operation of the Weyerhaeuser magnesium-base sulphite recovery system at Longview.

Over this period the plant operated at a rate equivalent to 322 air-dry tons of unbleached, unscreened, unknotted pulp per day. The pulp produced during this period had a bleachability equivalent to a permanganate number of 13 as established by TAPPI standards and had the other characteristics required for the production of high-quality, bleached paper-grade pulp.

The survey included (1) the measurement and analysis of the finished acid from the acid plant to the acid storage tanks (2) the measurement and analysis of the concentrated "red" liquor to the furnaces which was checked by measuring the flow from weak liquor storage tanks to the cascade evaporators, (3) the measurement of magnesium oxide and sulphur required for make-up, (4) the measurement of steam generated by the furnaces and boilers at 621 p.s.i.g., 715°F. and (5) the establishment of the losses of total solids from the system including organics, magnesium oxide, and sulphur.

During this survey we compared weak liquor flow to the evaporators with concentrated liquor flow to the furnaces and these when checked against steam produced established that during this period there were 2100 pounds of total solids per air-dry ton of pulp available for burning in the furnaces.

In addition to this we found that during this period we had lost the following quantities of solids per ton of air-dry pulp at pertinent points in the system.

	Organics	*MgO*	*Sulphur*
Vents at dump tanks	...	...	4.0
Knotters	6.0	0.5	0.7
Pulp leaving 3rd washer	73.1	8.7	13.0
Evaporators—acid condensate	9.3	0.6	0.8
Evaporators—jet condenser	150.0	17.8	17.7
Acid settling tank	...	0.2	0.1
Backwashing acid filters	...	2.5	6.0
Sewer	9.0	4.1	1.1
Total known losses	247.4	34.4	43.4

Over this period it was necessary to add 36.9 pounds of magnesia and 90 pounds of sulphur as make-up per air-dry ton of pulp, and also there was an inventory change at various storage tanks which was equivalent to adding 2.1 pounds of magnesia and 3.7 pounds of sulphur per ton to the system. This inventory change plus the actual make-up shows that there was a total make-up of 39.0 pounds of magnesia and 93.7 pounds of sulphur per ton.

Using 2100 pounds of total solids per ton at the furnace as a basis with an average heating value of 6060 B.t.u. per pound of dry solids as determined over the past year's operation, we find that when firing at an average concentration of 59% solids we generated 7915 pounds of steam per ton at 621 p.s.i. and 715°F. total temperature. In addition the hot gas from the boiler evaporated 1110 pounds of water per ton from the liquor in the cascades and heated 75,000 pounds of water per ton from 100 to 140°F. in the cooling towers.

As the second step in our presentation we will attempt to estimate a balance which is feasible and economically attainable by minor changes to the present system at Longview. To establish this new possible balance we will use as a basis the foregoing tabulation of known losses together with the experience obtained while operating the several pieces of equipment.

First, the loss of sulphur at the dump tank vents, which is in the form of SO_2 vapors, can be saved by collection in a suitable header and transferred to the cooling towers and subsequent absorption towers where it will be absorbed in conjunction with the SO_2 from the recovery units to make raw acid. At the present time we are installing a suitable header and line from these units to the cooling towers and in the future these vapors will be recovered.

Second, the losses of solids at the knotters, though small, are subject to reduction and should be considered. A suggested way to reduce these losses would be to crush the knots and wash them in a small diffuser and return the effluent to the proper stage of washing. Since this loss is so small, we are not at present planning to recover this loss but suggest that it should be considered in any subsequent proposals.

SVARRE HAZELQUIST, Pulp Division, Weyerhaeuser Timber Co., Longview Wash., and C. E. ROGERS, Babcock & Wilcox Co., New York, N. Y. Presented at Superintendents, Western Branch CPPA, and Pacific Section TAPPI meeting, Seattle, Wash., May 13, 1950.

Third, the losses of solids in the pulp leaving the third washer are of such magnitude that they deserve careful consideration. There are two feasible ways to reduce these losses. First, the most obvious way is to use more water for washing on the third stage. However, this method means more dilution of the filtrate and lower concentration of the liquor to the evaporators with more steam required for evaporation. The economics of this method of saving organics and chemicals will depend upon a comparison between the value of the recovered solids and the increased cost of evaporation. These losses also could be reduced by installing a fourth-stage washer, using the same total quantity of water for washing and, by control, maintaining dilution in the first-stage filtrate at its present low figure. At the moment we are considering using the existing brown stock washer at Longview as the fourth-stage washer and returning the filtrate for use in third-stage washing.

Fourth, the losses of solids in the acid condensate from the multiple-effect evaporators are due somewhat to mechanical carryover in the vapors from the several effects. However, there will always be losses in organics and sulphur which are inherent in the process of evaporating liquor derived from sulphite cooking. At the present we are considering ways and means to reduce the losses from mechanical carryover.

Fifth, the majority of the solids, particularly organics and magnesia, which are lost with the vapors from the fifth effect of evaporation to the jet condenser are due to mechanical carryover and can and should be saved. Since the survey we have made some changes to the evaporator which have reduced this carryover considerably and subsequent changes will further reduce these mechanical losses.

Sixth, the losses at the acid settling tanks are very small and probably inherent in the process since calcium entering the system with the chips will necessarily drop out at this point as a calcium monosulphite together with some magnesium compounds which are also insoluble. Therefore, we are not considering the elimination of these losses in the settling tank at Longview.

Seventh, the sulphur and magnesia loss at the acid filters is largely due to the residual acid left in the sand bed at the time of backwashing and besides this loss there is the inherent loss due to calcium monosulphite. The loss due to the residual acid could be reduced by flushing the bed with fresh water before backwashing and returning to effluent either to the settling tank or back to the absorption tower system. However this plan requires more time for backwashing and may require additional filter beds. We are considering this idea at Longview but are not planning to do anything definite in the immediate future.

Eighth, the losses of chemicals and organics to the sewer can be and are being eliminated except for unavoidable and infrequent tank spill-overs owing primarily to lack of adequate storage or capacity at certain stages in the system.

Having indicated the proposed methods for reducing the known losses we will now consider the possibilities of reducing or eliminating some of the unaccounted for losses which are small in the case of magnesia but higher and less subject to reduction in the case of sulphur which exists mainly as gaseous SO_2. Some of the more obvious unaccounted for losses are as follows. (1) Digester relief and filling losses which are small and in the form of sulphur dioxide do not lend themselves to any economic method of reduction in our case. (2) Sulphur lost in the vapors from the vents of the multiple-effect evaporators can be recovered by extending the vents to the cooling towers and absorption towers. At the present time we are connecting these vents to the vent line between the dump tanks and the cooling towers as outlined above. (3) Sulphur and magnesia lost as a deposit in the bottom of the absorption towers could be recovered in a large part by constructing the tower with conical bottoms instead of flat bottoms. This construction would insure that the magnesium monosulphite be kept in circulation through the towers thereby reducing its formation and increasing the production of the bisulphite. (4) Losses of chemicals due to sampling the liquor and acid are difficult to eliminate but could be reduced by installing return lines from the several sampling stations to allied equipment. For instance the concentrated liquor sampling at the pressure effects could be returned continuously to the vacuum effects of the multiple-effect evaporators. (5) The loss of magnesia at the experimental washer for removing potassium and sodium salts from the ash will be eliminated, of course, when we install a washer large enough to handle the system rate of flow. (6) The sulphur lost at the cascade evaporator level control tank will be recovered when the tank is sealed and vented to the gas duct between the boiler outlet and the cascade. (7) The sulphur lost to the stack is in the form of sulphur trioxide contained in the gases from the recovery unit. This loss can be substantially reduced by maintaining low excess air for combustion in the recovery units but cannot be eliminated entirely. (8) The sulphur lost as sulphur trioxide in the SO_2 gas coolers in the acid plant cannot be eliminated but in any case the amount is small, probably less than 0.5 pound per ton. (9) The sulphur lost with the vapors from the vents of the dilution and weak liquor tanks can be recovered if these vents were connected to the vent system to the cooling towers as outlined above. (10) Chemical losses of magnesia and sulphur by leakage at pump packing glands and at pipe fittings and valves are impossible to eliminate entirely but can be reduced to a large degree.

On the basis of the foregoing discussion of the proposed methods of reducing the losses of organics, sulphur, and magnesia in the recovery system as it is installed at present in the Weyerhaeuser mill at Longview, we can arrive at a material balance wherein the known losses have been reduced to economic levels. The following tabulation outlines what we believe to be the practical minimum of losses applicable to the present Longview operation in pounds per air-dry ton of pulp.

	Organics	*MgO*	*Sulphur*
Vents at dump tanks	0	0	0
Knotters	6.0	0.5	0.7
Pulp leaving 3rd-washer	31.0	7.0	11.2
Evaporators (acid condensate and jet condenser)	26.0	3.0	2.9
Acid settling tank	...	0.2	0.1
Backwashing acid filters	...	2.5	6.0
Sewer	0	0	0
Total known losses	63.0	13.2	20.9

Using the above tabulation of known losses and considering the recovery of the unaccounted for losses as impractical at this time, we find that under optimum conditions at Longview the make-up of sulphur would become 71.0 pounds per ton or an over-all sulphur recovery efficiency of 70%. The make-up of magnesia would become 18 pounds per ton or a recovery efficiency equivalent to 88%.

In addition we would find 2350 pounds of total solids per ton of air-dry pulp available for firing in the recovery furnace. With this fuel having an average heating value of 6060 B.t.u. per pound of dry solids and fired at an average concentration of 59% solids we would generate 9000 pounds of steam per ton at 621 p.s.i. and 715°F. total temperature.

In concluding we wish to emphasize that we have dealt only with the conditions and the recovery equipment as they now exist at the Longview mill and that we have considered the digester SO_2 recovery and the dump tanks as integral part of the installation.

We believe the findings of our survey would prevail at any future installation of a recovery system if similar in all respects to the Longview installation.

Further, for any other magnesium recovery installation which has been modified to include existing or projected blow

pit sulphur recovery systems, we believe the expected recovery of sulphur will depend upon the efficiency of the auxiliary system, as the efficiencies of the magnesium recovery which starts basically at the pulp washers will be essentially as developed at Longview.

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Chemical Cleaning of Black Liquor Evaporators

H. H. WALTHER

ESSENTIALLY, chemical cleaning is the use of liquid solvents to remove undesirable deposits or coatings that reduce the efficiency or effectiveness of process equipment. The paper industry is particularly well adapted to chemical cleaning as illustrated by the use of solvents in maintaining the efficiency of black-liquor evaporators. This article deals with the fundamentals of chemical cleaning and its application to paper mill equipment with emphasis on the cleaning of black-liquor evaporators.

Chemical cleaning depends upon three major factors: (1) the deposit to be removed; (2) the chemical solvent, and (3) the type of unit and material used in its fabrication. The deposit determines which solvents will be used. It must be fully understood before any operation is undertaken. Chemical analyses and solubility tests determine the deposits and the solvent. The types of deposits found in paper mill equipment are illustrated in Table I. The solvent generally used in paper mill cleaning work is sulphuric acid in various concentrations. It has the advantage of not requiring special equipment for storage and handling. Inhibited hydrochloric acid solutions with and without intensifiers make the best scale solvents and have been proved in other industries. Also, in the cleaning of black-liquor evaporators, oxidizing solutions have been found to be far superior to white liquor or various alkaline solutions of the common alkalies.

Table I. Types of Deposits Encountered in Paper Mill Equipment

Water deposited
Carbonates
Phosphates
Sulphates
Silicates
Corrosion products
Oxides
Sulphides
Organic-process side deposits
Oils
Polymerized oils
Decomposed-carbonized-organic

Black-liquor evaporators become fouled rather rapidly. Chemical cleaning, using preboils with white liquor followed by dilute sulphuric acid, has long been a part of their maintenance. The results obtained are only fair and corrosion has often resulted from the improper use of the dilute sulphuric acid. The results of investigations on a number of black-liquor-evaporators show the deposits to be mainly: calcium carbonate, silicates, oxides, and organics.

Inhibited hydrochloric acid will remove the calcium carbonate, the oxides, and the sulphides. Inhibited hydrochloric acid plus an intensifier will remove the silicates. Preboils with oxidizing solutions will attack the organics and convert them in such a manner that they can be removed with inhibited hydrochloric acid.

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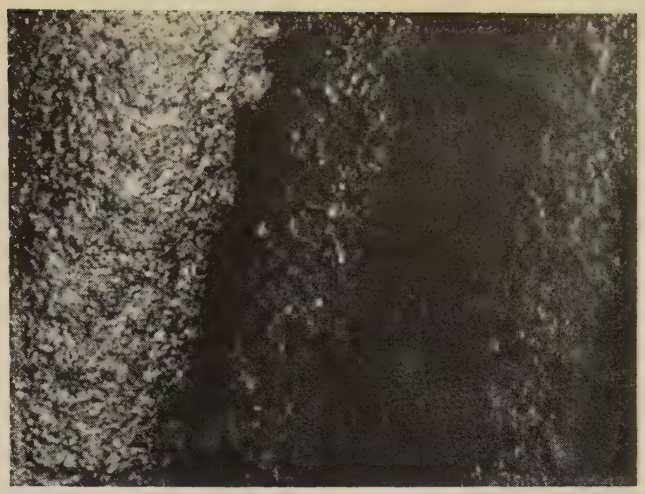

Fig. 1. Fifth effect evaporator after two years' operation

The tube side of black-liquor evaporators offers no particular problem as the solvent is pumped into the unit completely filling the tubes. Any scale that is not dissolved sloughs from the tubes and drops down into the bottom of the evaporator where it is easily washed out.

The shell sides of evaporators are not as readily cleaned. The problem is aggravated in that any deposit that sloughs from the outside of the tubes drops down upon the tube sheet where it piles up and is difficult to wash out because of the design of the units. The deposits which pile up on the bottom tube sheet are so thick that even were they readily soluble they would be difficult to remove because the solvent quickly spends itself within the mass and prevents the entrance of fresh solvent. On two known occasions concentrated sulphuric acid has been successfully used to remove the piled up deposit from the bottom tube sheet. This is a hazardous operation and not recommended, although with proper supervision it can be done safely.

The solution to the maintenance of the shell side of evaporators seems to be more frequent chemical cleaning operations. Figure 1 shows the outside of the tubes in a fifth effect evaporator after two years' operation. The deposits are heavy, almost $^1/_4$ inch thick. They are mainly sulphides, oxides, and organics. An oxidation solution followed by inhibited hydrochloric acid will attack and disintegrate these deposits. Figures 2–4 show deposits on the outside of second-, third-, and fourth-effect evaporators that have been in operation only 1 year. Here the deposits are thin, less than $^1/_8$-inch

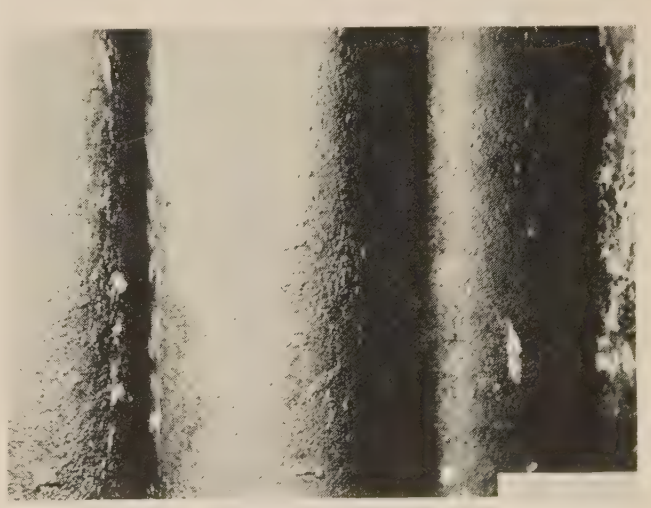

Fig. 2. Second effect evaporator after one year's operation

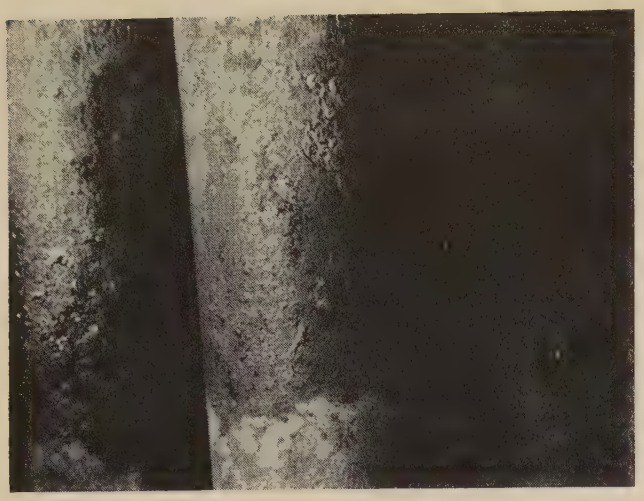

Fig. 3. Third effect evaporator after one year's operation

thick. These deposits are also sulphides, oxides, and organics. They also are readily attacked and dissolved by an oxidizing solvent followed by inhibited hydrochloric acid. Due to the comparatively small amount of deposit present, there is no piling up of the deposit on the bottom tube sheet. The material that sloughs is in fine particles and remains suspended in the solvent, and is readily pumped from the units. The solution to keeping the shell sides clean seems to be regular chemical cleaning at 9- to 12-month intervals.

A large kraft mill in the State of Virginia operates two sets of Swenson long-tube, multiple-effect evaporators. In both sets it had been necessary to re-tube the last four effects approximately every four years due to deposits piling on the tube sheet to a depth of 6 feet at the center. And, as previously stated, the deposits which piled up on the bottom tube sheet were so thick that even if they were readily soluble they would be difficult to remove because the solvent would quickly spend itself within the mass and prevent the entrance of fresh solvent. This takes place even though white liquor is boiled for 24 hours at 6-month intervals.

A study of possible results using chemical cleaning on a time cycle basis was made. It was felt that if the units were cleaned from nine months to a year after retubing, efficiency could be maintained and tubes would give service to full life expectancy of the metal.

In June, 1948, effects Nos. 3, 5, and 6 of one set of evaporators were cleaned. Numbers 5 and 6 had been retubed nine months prior to this date and were found to be clean after chemical cleaning. Number 3 had been in operation for six years and although large amounts of deposits had been removed the operation could not be considered entirely successful.

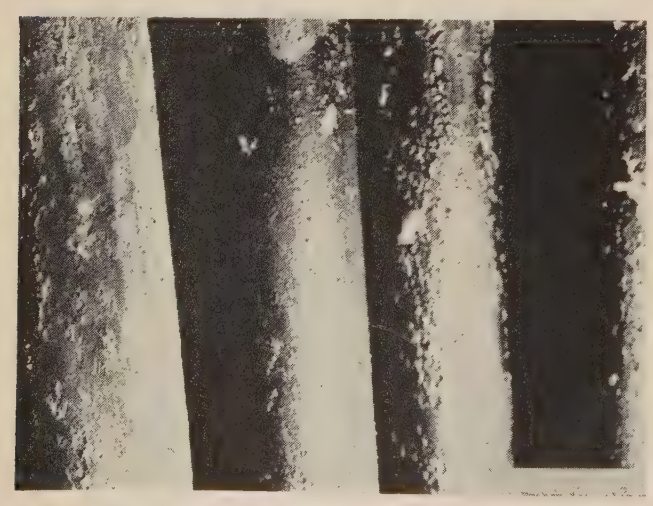

Fig. 4. Fourth effect evaporator after one year's operation

In October, 1948, Nos. 3–7 effects of the second set were chemically cleaned. This set had a rated capacity of 220,000 pounds evaporation per hour and was down to approximately 155,000 pounds evaporation per hour. Chemical cleaning increased the evaporation approximately 30,000 pounds per hour.

In June, 1949, all of these units were cleaned again. The second set had never attained rated capacity and an investigation by the operating company disclosed deposits at the center of some of the tube bundles. It is believed the lack of chemical cleaning of these units since their retubing three years before was responsible. By contrast, the first set has been operating at rated capacity continuously since 1948. The comparison of these two sets is convincing proof that efficiency can be maintained, thereby substantially reducing maintenance costs by periodic chemical cleaning every 9 to 12 months.

The use of inhibited hydrochloric acid solutions brings in the problem of special rubber-lined storage facilities for the concentrated acid, corrosion resistant pumps, and mixing equipment. This is readily solved by the use of the specialized mobile equipment used by service companies doing this work on a large scale. The hook-up is fairly simple as shown in Fig. 5. The proper identification of deposits and the choice of correct solvents require an experienced engineer.

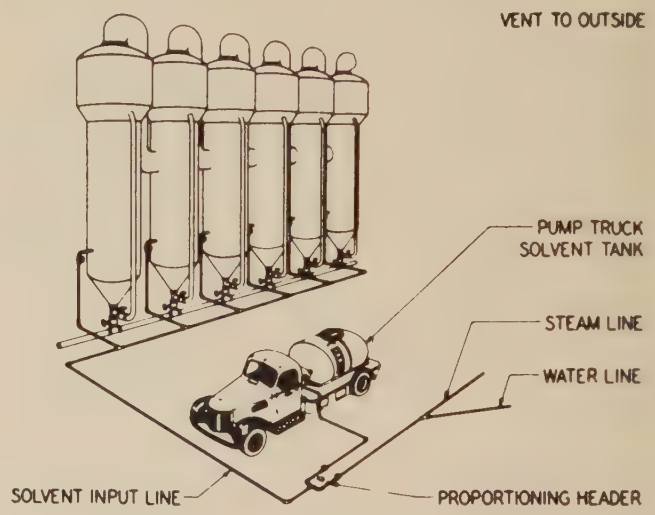

Fig. 5. Hook-up used in cleaning black liquor evaporators

Existing connections can be used for solvent input and output lines. Steam is required for preheating the solvent, and water is required for dilution of the concentrated solvents. A set of four to six effect evaporators can be readily cleaned in a day's time.

Chemical cleaning is not confined to evaporators. Its extensive use in other industries has resulted from the cleaning of thousands of pieces of equipment including boilers and associate equipment such as economizers, superheaters, and feedwater heaters. Tube and shell units, large surface condensers, pipe lines, and practically all types of heat-exchange equipment are readily cleaned chemically. Inhibited hydrochloric acid properly used can also restore water wells to normal flow when production has decreased due to fouling of the formation or screen.

Chemical cleaning is in reality a maintenance tool which allows the engineer to maintain production by decreasing down time, replacement, and repair costs in his mill. Typical chemical cleaning operations in paper mills are shown in Table II. By recognizing the problems involved and thoroughly understanding proper applications, chemical cleaning is without a doubt the easiest and most economical aid to

Table II. Typical Chemical Cleaning Operations in Paper Mills

Location	Unit	Deposits	Procedure
Virginia	3-250 Hp. HRT boilers	Approximately $^1/_4$-in. of calcium sulphate and calcium carbonate	Soda ash preboil followed by dilute acid-base solvent; 14 hr. time
Michigan	556 Hp. Heine water tube boiler and economizer	$^1/_{32}$–$^1/_5$-In. calcium phosphate plus silicate	Fill with dilute acid-base solvent at 160°F. Soak 6 hr.: 6 hr. time
Pennsylvania	500 Hp. B & W two-drum boiler and superheater	Calcium phosphate	Fill with dilute acid-base solvent at 150°F. Soak 6 hr.: 8 hr. time
Michigan	Economizer on 765 hp. Foster-Wheeler boiler	Calcium carbonate and iron oxides	1000 Gal. dilute acid-base solvent pumped through economizer at 155–160°F. discharging to sewer: 7 hr. time
Virginia	C.E. 100,000 lb./hr. recovery boiler	Silicates	Alkaline boil plus acid 24 hr.
Michigan	Three-effect black-liquor evaporator, both tube and shell sides	Mixture of iron oxide, iron sulphide, and silicates	Fill three effects simultaneously with dilute acid-base solvent at 150–160°F.: 10 hr. time
Wisconsin	Shell sides of three-effect Swenson	Mixture of iron oxide, iron sulphide, and silicates $^1/_{32}$–$^1/_8$-in. thick	Fill shell sides with dilute acid-base solvent at 160°F.
Michigan	Two small tube and shell condensers, anthracite filters	Thick calcium carbonate	Dilute acid-base solvent pumped through condenser to filters: 3 hr. time
Virginia	C.E. 200,000 lb./hr. boiler	$^1/_{16}$-In. silica and iron oxide	Turbining impossible two stages acid: 24 hr.
Michigan	Water well, 40 ft. of 36-in. casing, 15 ft. of screen	Calcium carbonate and iron oxides on screen and pump	2000 Gal. 20% inhibited hydrochloric acid: 8 hr. time
Maryland	Small feedwater heater on tube side	Approximately $^1/_2$ in. of calcium carbonate	500 gal. of dilute acid-base solvent pumped through heater: 6 hr. time
New York	875 ft. of 8-in. pipe handling pulp slurry	$1^1/_4$–2In. thick, mostly calcium carbonate	Filled line three times with dilute acid-base solvent, washed with water. Line cleaned annually
Texas	Waste heat condenser. Both tube and shell side	$^1/_{32}$-In. calcium carbonate on tube side. Thick organic sludge	Oxidizing solution on shell side followed by acid-reducing solution. Acid-base solvent in tube side: 8 hr. time
Louisiana	Two 750 hp. boilers, two 1000 hp. boilers	$^1/_8$–$^1/_4$-In. hard silicate	Could not turbine. Two alkaline stages and two acid stages cleaned boilers
Illinois	24 Processing rolls	$1^1/_2$-In. calcium carbonate	750 gal. 7% hydrochloric acid, 6 hr., all scale removed
Virginia	Seven effects Swenson evaporators	Sulphides, iron oxides, silicates, organics	Oxidizing solution followed by acid: 24 hr.
Virginia	Three 1088 hp. B & W boilers	Silicates, iron oxides	Alkaline boil—followed by acid: 24 hr.

efficient production and maintenance readily available to paper and paper products manufacturing plants. Correctly applied chemical cleaning can become one of the most valuable tools in the paper industry.

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Presented at the Annual Meeting of the Technical Association of Pulp and Paper Industry, New York, N. Y., Feb. 20–23, 1950.

DISCUSSION

PETER B. BORLEW (Container Corp. of America): At one point you mentioned an inhibitor and an intensifier. Can you use both successfully at the same time?

MR. WALTHER: Yes. The inhibitor is used to slow up the corrosive action on the metal itself, while the intensifier is employed to speed up and intensify the reaction on the scale.

S. FOSTER (Kalamazoo Vegetable Parchment Co.): When you have a 3 and 4-foot deposit in the bottom of the evaporator body, do you believe this deposit can be cleaned out and kept out by frequent cleaning?

MR. WALTHER: Yes. As a further refinement, it has been suggested that a center tube, with holes, be used to clean this deposit out. Such holes would be spaced around the tube connected to a source of high-pressure water. Naturally, means would be employed to blank off this one tube when the evaporator was in use.

MR. FOSTER: What would be the cost of cleaning an evaporator installation producing almost 200 tons of pulp per day?

MR. WALTHER: The cost will vary, depending on the severity of the scale, but will approximate $250 to $400 per body.

J. SCHWARTZ (Howard Smith Paper Mills Ltd.): You have mentioned cleaning the outside of the tubes, but what about cleaning the inside of the tubes. I feel that this is just as important as the outside. Also, I have personally felt that inhibited HCl will attack the steel and so hesitate to use this treatment too often.

MR. WALTHER: There should be very little trouble in cleaning the inside, which should be done every time the bodies come off. Also, there are many inhibitors, on the market, some better than others, therefore the amount of attack is dependent on the inhibitor used. I believe that a satisfactory inhibitor will protect the steel tubes during the acid treatment.

M. L. OLIVER (Continental Can Co.): Perhaps it would be of assistance to Mr. Foster to say that we have found that the prime requisite of removing the loose scale piled up on the tube sheet, is a quick flushing. Accordingly, we have had our clean-out doors fitted with but one bolt which permits of quick opening during this cleaning. By this method we flush out each body quickly, the fast gush of water carries with it much of the loose scale piled up on the bottom of the tube sheet.

EMPLOYMENT SERVICE

Positions Wanted

E79-50. Chemist with experience in papermaking and coating desires position with progressive paper company.

E80-50. Physicist, 28 years, married, one year pulp and paper-mill experience on variety of research problems. 1949 college graduate.

E81-50. Chemical engineer, 34. Ph.D. 6 years as research director, 4 years as group leader in process development in chemical field. Prefer southern location.

E82-50. Asst. superintendent. Plant manager desires change. 21 years' experience covering board, book, news, pulping, various papers. Has specialized in tissue research and development last 6 years. College graduate.

E83-50. Chemical engineer, M.S. 8 years' experience research, technical control. Paperboard, coatings, adhesives, cartons, containers. Desires position in converting or allied industries east or midwest.

E84-50. Chemical engineer, B.S. degree, 27, married. Experienced in quality-control work. Desire similar position or that of paper or pulp mill chemist or engineer.

E85-50. Man with following qualifications in paper industry desires permanent position: Married, 47, production superintendent corrugated box shop, paper and container research, packaging engineer with Signal Corps and Army food research, some travel satisfactory.

Positions Open

P78-50. Paper research chemist. Established organization desires research man for laboratory engaged in development of speciality products, Ph.D. desirable but not essential. Give details of education, experience, and salary requirements. Location New York City.

P79–50. Quality control man, with experience and responsibility desired by integrated pulp and paper mill in New England.

P80-50. Young man, preferably technical graduate with actual production experience in papermill, wanted for responsible sales and technical service position involving filler and coating clay. Considerable traveling from New York office.

P81-50. Young engineer with from 3 to 5 years' experience in pulp and paper-plant operation. Opportunity involves basic training in industrial equipment leading to promotional effort in the pulp and paper industry.

P82-50. Superintendent for three machine and groundwood mill, located in Northeast. Technical background desirable but not necessary. No capital necessary.

Developing Executive Talent

Ralph J. Cordiner, Executive Vice-President of the General Electric Co., speaking at the 18th annual meeting of the Edison Electric Institute, stated that developing executive talent is industry's most challenging problem. This problem is posed chiefly by the recent rapid growth of industry, demanding more management personnel, and the age of specialization, which tends to sacrifice the broad outlook necessary for good management.

"We cannot govern industry today with nothing but a group of specialists at the top, unless we are prepared to call a committee meeting every time there is a management decision to be made."

As a solution he suggested building "second and third teams" of reserve executives under executive development programs. He said such programs should include regular rotation of selected specialists on jobs of different nature, establishment of more assistant-managerial jobs, writing of managerial job descriptions to help determine qualifications, off-the-job management training, and periodic review of such programs by the chief executive.

Comparing today's executive to the family doctor, Mr. Cordiner said the present-day manager knows his business because he has been with it "through its labor pains, its growing pains, and in place of measles and mumps, two world wars, and a depression."

His successor, however, must come from the ranks of specialists, whose specialities have narrowed their outlook and who have not had natural opportunities to exercise leadership, he added.

"Companies for a long time have done a good job of recruiting and early training," said Mr. Cordiner, but "too often, at the most critical period in the development of an executive, we have neglected to provide any opportunity for training at all.

"We suddenly find ourselves doing one of two things: We take the man who has been specializing during some of the most important formative years of his life and give him a title, saying, 'now, you're a manager.' Or we find ourselves saying, 'we'd like to promote a man from within the ranks, but none of them has the proper qualifications.' "

As remedies for the executive dearth, Mr. Cordiner sugested first a regular rotation of selected specialists on jobs of different nature but warned that opportunity for delegation of authority must be a part of such jobs.

A means of accomplishing this, he continued, would be the second remedy, that of establishing assistant manager and assistant-to-the-manager jobs, which would be concerned not just with the specialties involved but with over-all managerial aspects.

Such jobs should permit learning "how to select people and organize their efforts by defining responsibility, authority, and accountability," learning the "understanding of human relations," and developing "sensitivity to social, economic, and political trends," he indicated.

The G-E official said that "writing job descriptions of the present managerial positions will help determine what qualifications are needed to fill them and will pave the way .... for selection of replacement candidates."

Another device helpful toward this end, he siad, is the organization chart, which, if put to work, "provides a road map for an executive development program," which, "like any good road map, shows you both where you are and where you want to go."

Mr. Cordiner pointed to the Harvard School of Business Administration's 13-week course in advanced management as illustrative of off-the-job training, and said success of this course and others is evidence of the number of companies now using this method.

To make sure that any executive development program is carried out effectively, such a course should be the concern of the No. 1 executive of a company and should call for periodic review of the program by the top executive and other officers.

LETTERS TO THE EDITOR

Mill and Laboratory Beaters

The following letter was addressed to the Secretary of the Australian Pulp and Paper Industry Technical Association and appeared in the APPITA News Letter, April, 1950. It is reproduced here for its information value.

The Secretary, APPITA.

So much excellent work has been done in Australia on beating and refining problems, that it seems a pity that Dr. Cohen's suggestion on page 130 of Vol. 11 of the Proceedings, to compare results on a basis of sheet density rather than freeness, is not more widely accepted.

May I suggest that those who believe that freeness, is a valid measure of "degree of beating" or "hydration," carry out the following simple experiment which only takes a few minutes in a paper mill?

Take some raw pulp and some mill-prepared stock from the machine chest and obtain their freenesses in the usual way. For example, with southern pine kraft, I obtained freenesses of 760 and 550 ml. on a Schopper Riegler with a 5-gram sample from a machine making liner board. Then make another freeness test with the raw pulp but instead of using fresh water for diluting the sample to 1000 ml., use white water caught from beneath the fourdrinier wire. In my case I got a result of 345 ml. In other words, the simple addition of white water immediately imparted to the raw pulp a high degree of beating, in fact a splendid kind of hydration—the kind without cut fibers.

Unfortunately, burst tests made on sheets prepared from the raw pulp, with and without white water, showed no sig-

Table I. Comparison of the Actions of the Sutherland Refiner, Valley Beater and Clark Kollergang on Southern Pine Kraft.

	Sutherland Refiner	*Valley Beater*	*Clark Kollergang*
Density—g./cc.	0.65	0.65	0.65
Freeness—°S.R. 5 g.	630	660	675
Burst factor—metric	55	67	53
Tear factor—metric	130	150	145
Tensile breaking length m.	8,120	8,730	7,800
Zero-span breaking length —m.	15,400	15,500	15,300
Percentage stretch	3.1	3.3	3.2
Specific surface—cm²/g	15,500	13,000	14,000
% retained on 14 mesh	48	53	42
% through 14—on 28	21	22	31
% through 28—on 48	13	13	16
% through 48—on 100	4	4	6
% through 100—debris	14	8	5
Weighted average fiber length—mm.	2.71	2.93	2.80
Approx. power or time	150 kw. hr./ton	20 min.	15 rev./ g.

nificant difference, as was also found by Morris and de Montigny; see Proc. Tech. Sect. Canadian P. & P. Assoc. 1940, pp. 46–51; Pulp Paper Mag. Canada 41, no. 2; 107–112 (Feb., 1940).

To indicate how important is the choice of a basis of comparison of stock, compare the conclusions of A. J. Laugher from Table II, page 171 of Vol. 11, part of which was reproduced on page 732 of Paper Industry and Paper World of Sept., 1949, with those deducible from the attached Table I. These are recent data from southern pine kraft obtained in accordance with TAPPI Standard Methods. The three stocks are compared at a density of 0.65 gram per. cc. which is equivalent to a fairly good degree of beating for this pulp for board.

My objection to the use of a miniature beater for treating pulp for testing is simply that it is utterly impossible to standardize a sharp cutting edge. The edges can't be rounded because even with the normal sharp edges, unless the consistency of the pulp is lowered to about 0.7% and the normal roll pressure doubled (which procedure would quickly change the cutting edges) a miniature beater can't simulate the cutting action of the massive mill machines. The reduction of freeness which is secured, is the result of gently fibrillating almost every fiber and separating some of the particles, whereas in practice the main cause of the freeness test going down with beating is the production of very fine debris derived from the smashing apart of only those fibers hit by the massive bars of the mill equipment.

The laboratory kollergang simulates the heterogeneous cutting action of the heavy mill equipment; however the smashing action is absent to produce enough debris to affect the freeness very markedly, but it nevertheless does produce a stock which is fairly close to mill-beaten pulp as far as tangible sheet characteristics are concerned. Obviously, if one wanted to simulate the action of laboratory beaters or refiners, which, it should not be forgotten, are highly arbitrary and unique pieces of equipment, all one would need to do to a laboratory kollergang would be to greatly reduce the weight of the rolls. This would make a cheaper and nicer instrument in many ways and would, because of the higher strength and lower freenesses developed with pulps, make the majority of investigators feel much happier with it. However, it would no longer then be an honest offering even although it would, as it admittedly does now, outperform every other piece of laboratory equipment for reproducibility.

Yours very truly,

James d'A. Clark
Box 996, Longview, Wash.

P.S.: May I add that I have no financial interest whatever in the sale of any piece of pulp or paper testing equipment.

RECENT BOOKS

The Strength of Plastics and Glass. By R. N. Haward, Research Chemist, Petrocarbon Ltd., Manchester, Eng. Interscience Publishers, Inc. New York. 1949. Cloth. $5\frac{1}{2} \times 8\frac{1}{2}$, 245 pages. $5.50.

A subtitle of this book is "A Study in Time-Sensitive Materials." It is concerned primarily with the mechanical properties of plastics and glass of interest to engineers and scientists working on such materials. Among the subjects covered are strength relations, static strength, deformation of plastics and glass, hardness and related subjects, impact strength, and some characteristic properties of complex materials. Much experimental data is given. Theoretical considerations are limited to possible explanation of some of the experimental results.

Industrial Experimentation. 3rd American Ed. By K. A. Brownlee, London, Eng. Chemical Publishing Co., Brooklyn, N. Y. 1949. Cloth. $5\frac{1}{2} \times 8\frac{3}{4}$, 194 pages. $3.75.

This is a monograph intended to be a guide to both the planning and the interpretation of experiments on the industrial scale. It was released by the British Director of Ordnance Factories (Explosives), Ministry of Supply. It is suggested that the practice of consulting a statistician only after the experiments have been completed should be condemned. The methods outlined are recommended as a standard tool for establishing tests of significance. Among the subjects covered are fundamental statistical conceptions, significance of means, comparison of variances, the Poisson Distribution, quality control chart, correlation between variables, etc. A fair mathematical background is needed to understand this subject.

Encyclopedia of Chemical Reactions. Vol. III. Compiled and edited by C. A. Jacobson, Professor of Chemistry Emeritus, West Virginia Univ. Reinhold Publishing Co., New York. Cloth. 6 × 9, 842 pages. $12.

This is the third volume in a series intended ultimately to embrace the published reactions of the active chemical elements and their simpler compounds. It covers the elements from cobalt to iridium inclusive. The work of compiling this information is being carried on by 118 abstractors. The detail involved in this work is represented by the 822 reactions of cobalt alone.

Industrial Hygiene and Toxicology. Vol. II. Edited by Frank A. Patty, Director, Industrial Hygiene Service, General Motors Corp. Interscience Publishers, Inc. New York. 1949. Cloth. $6\frac{1}{2} \times 10$, 1138 pages. $15.

This is the second of two volumes on this subject and is the work of 18 authorities. It describes the effects of exposure to industrial chemicals. Among the subjects covered in this volume are industrial hygiene records, survey of personnel, personal factors in competence and fatigue, mode of entry and action of toxic materials, sampling and analysis of atmosphere contaminants, ventilation, occupational dermitoses, fire and explosion hazards, alkaline materials, the metals, organic acids, phenol compounds, etc. The book should find considerable use in mill hospital service departments.

Copies of all books reviewed in this issue may be obtained through the Book Dept., Technical Association of the Pulp and Paper Industry, 122 East 42nd St., New York 17, N. Y.

Instrumentation Studies. LVI. Penetration of Paper by Water Vapor

Part VIII. Development of a Method for the Measurement of Water-Vapor Permeability at Low Temperatures

W. A. WINK and J. A. VAN DEN AKKER

This report describes the development of a method for the measurement of water-vapor permeability at low temperatures in which the application of the dynamic method has been investigated. The dynamic method was developed in an earlier instrumentation study for the measurement of permeabilities at normal room temperatures and was described in Instrumentation Studies LII (*1*) and LIII (*2*). Studies which are pertinent to the field of permeability measurements at low temperatures and which are described in this report include: (1) the development of a cryostat for the control of temperatures and relative humidities, (2) an investigation of the performance of the electric hygrometer at low temperatures, (3) the design and development of the permeability testing apparatus applicable to low-temperature work, (4) the evaluation of equilibrium relative humidities over saturated salt solutions, (5) the development of an indirect method for obtaining the moisture absorptive capacity of the electric hygrometer at both normal room and subfreezing temperatures, and (6) the development and performance of a small electric hygrometer, in which the moisture absorptive capacity is appreciably reduced. Following the successful development of a small electric hygrometer having a low moisture-absorptive capacity, permeability measurements were made by the dynamic method at a reduced temperature employing samples of pliofilm and polythene. The permeability measurements on these two samples have shown that the dynamic test is a rapid method for evaluating the water-vapor permeability of moistureproof materials having a low moisture absorptive capacity.

PAPERS DESIGNED to resist the passage of water vapor at low temperatures have received considerable attention in recent years. It is apparent from their use as a protective and packaging medium for frozen foods that the water-vapor transmission rates and a method of evaluating these rates are of interest. Consequently, it was considered advisable by the Subcommittee on Instrumentation Research of the American Paper and Pulp Association to include in the instrumentation program a study, the objective of which was the development of a means for evaluating the water-vapor permeability of papers at low temperatures. It is the purpose of this report to present the work carried out to date on such a method.

The selection of a method applicable to permeability measurements at reduced temperatures could conceivably be any one of the existing methods currently employed for obtaining permeability data at room temperatures. The problem involved in the development of a method is primarily one of adaptation. After consideration of the various methods, it was believed the recently developed "dynamic" method, which employs the electric hygrometer, warranted investigation. The dynamic method for evaluating water-vapor permeability at normal room temperatures was developed in an earlier phase of the instrumentation program and is fully described in the current series of reports on water-vapor permeability (*1*, *2*).

A desirable attribute of the dynamic method is its high sensitivity. The need for a highly sensitive method is particularly evident when consideration is given to the unusual conditions under which the permeabilities are to be measured. For example, let us compare the vapor pressure differences obtaining at 100°F. under typical permeability testing conditions with those obtaining at 0°F., where, in each case, the two surfaces of the test specimens are exposed, respectively, to relative humidities of 0 and 90%. The corresponding vapor pressure differences across the test specimens are 44.2 and 0.86 mm. of mercury for temperatures of 100 and 0°F., respectively; the ratio of the two pressure differences is 51 to 1. If we now assume, for illustrative purposes, that the rate of transfer of water vapor through a test specimen is proportional to the difference in the partial pressure of water vapor at the two surfaces, then the rate of transfer of water vapor at 0°F. should be $^1/_{51}$ of the transfer rate at 100°F. It is apparent that the transfer rate of water vapor for specimens of good moistureproofness will be quite low at 0°F. For a good moistureproof specimen having a permeability rate of 0.25 gram per 100 square inches per 24 hours at 100°F., a transfer rate of only 0.005 gram per 100 square inches per 24 hours at 0°F. might be expected.

The application of an existing method to the measurement of water-vapor permeability at reduced temperatures involved a study of factors on which pertinent information to date is quite limited. It was necessary, therefore, to include in the pursuance of the objective of this study the following: (1) A study of the performance of the electric hygrometer at the reduced temperatures and the development of techniques for handling the hygrometer to avoid moisture condensation difficulties. (2) The development of a method to control the relative humidity at the reduced temperature. Controlled temperature and relative humidities are required in the establishment of a controlled vapor pressure gradient across the two surfaces of the test specimen. (3) A study of the moisture absorptive

W. A. WINK, Technical Associate; and J. A. VAN DEN AKKER, Research Associate, The Institute of Paper Chemistry, Appleton, Wis.

capacity of the electric hygrometer and the adsorptive capacity of the surfaces disposed to the test space in the dynamic method. The absorption and adsorption of moisture by a material or surface in the test enclosure are factors which influence the dynamic rates and must be taken into account in calculating the water-vapor permeability of a specimen. (4) The design and development of a permeability testing apparatus suitable for use at low temperatures.

DEVELOPMENT OF METHOD FOR CONTROLLING TEMPERATURE AND RELATIVE HUMIDITY

A schematic cross-sectional view of the cryostat in which the low-temperature phases of this study were carried out is shown in Fig. 1. The cryostat was designed to provide sufficient flexibility so that, with slight modifications, it could be used for the measurement of water-vapor transfer rates, the calibration of the electric hygrometers, and the observation of sorption data.

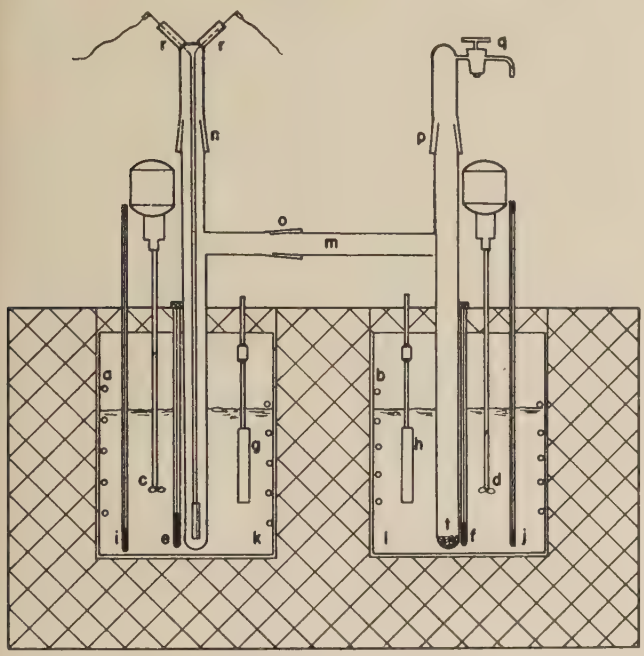


Fig. 1 Cryostat

The main body of the cryostat was constructed of Foamglass blocks 5 inches thick. A heavy grease was used as a vapor seal between adjacent blocks of insulation and the entire boxlike structure was held together by means of a wooden frame and two steel bands. The cover of the cryostat was constructed of a 1-inch asphalt-coated fiber insulation board; it was split longitudinally at the center to provide access to the equipment in the cryostat.

Two rectangular galvanized sheet iron tanks, 18 inches long, 12 inches wide, and 12 inches deep, provided the means for holding the bath liquid, which was Sólox, a commercial grade of ethyl alcohol. The baths were equipped, respectively, with cooling coils (a and b), motor-driven stirrers (c and d), mercury-to-platinum type thermoregulators (e and f), knife type electric heaters (250-watt, 220-volt) (g and h), and thermometers (i and j).

A 0.25-hp. refrigeration compressing unit (using Freon No. 12 as a refrigerant) was employed for cooling the baths. A schematic diagram, showing the arrangement of the cooling coils and the relative location of the various types of valves employed in the refrigerating system, is presented in Fig. 2. The cooling coil in each

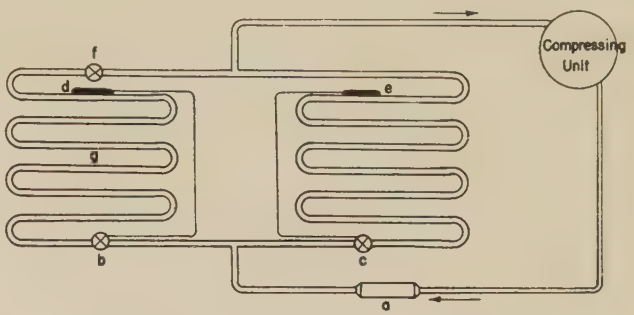


Fig. 2 Cooling system

bath consisted of approximately 50 feet of $^3/_8$-inch copper tubing bent into an oval helix so that it fitted closely against the walls of the galvanized tanks. Referring to Fig. 2, the refrigerant (Freon No. 12) was fed to the cooling coils through a dryer tube (a) to the thermostatic expansion valves (b and c) (Frigidaire Modulox valves having a rated capacity of 3000 B.t.u. per hour). The thermostatic elements (d and e) of the respective valves were fastened to the last turn of the cooling coils inside the cryostat. Located outside of the cryostat and at the end of the cooling coil employed to cool the warmer bath was a constant pressure valve (f) (an Alco Evapotrol pressure regulator with an adjustable pressure range from 11 inches of mercury to 30 p.s.i.). This valve controls the refrigerant pressure and, consequently, the temperature of coil g of Fig. 2.

For the present work, the left bath (k of Fig. 1) was used essentially as a constant temperature bath and was controlled for the various phases of the study at either −18.0°C. (nearly 0°F.) or at −12.2°C. To maintain either of these temperatures, the constant pressure valve was adjusted to give a coil temperature just slightly less than that required to cool the bath to the desired temperature. By means of the knife heater, operated by the thermoregulator, the bath was controlled at the desired temperature. Since the 250-watt, 220-volt heater was operated at 110 volts, only 25% of the effective power of the heater was expended in controlling the temperature of the bath. With the constant pressure valve adjusted so that the on-off time intervals of the heating cycles were approximately equal, the over-all variation in bath temperature was held within 0.02°C.

The bath l (Fig. 1) was primarily used for controlling the partial pressures of water vapor over ice. It was necessary to have the control range temperature of this bath variable so that temperatures down to −36.0°C. could be obtained. The manner of temperature regulation of this bath was determined by the nature of the experiment. When the cryostat was employed for calibrating single electric hygrometer elements, it was found expedient to regulate the temperature manually.

With the compressing unit operating continuously, the superheat setting of the expansion valve was adjusted so that the cooling coil maintained a bath temperature just below the desired temperature. The temperature of the bath was raised to the desired point by adjusting the voltage supplied to the heater by means of a variable autotransformer connected with the knife type heater.

When the cryostat was employed for experiments which required a constant temperature over an extended period of time, the temperature of this bath was regulated in essentially the same manner as that of bath k. The superheat setting of the expansion valve was merely adjusted to admit sufficient refrigerant into the coil to maintain a bath temperature slightly below the desired temperature. The thermoregulator in control of the knife heater then maintained a bath temperature well within 0.02°C. In experiments involving frequent changes of the bath temperature, such as the simultaneous calibration of several electric hygrometers, it was found desirable and expedient to start the experiment at the lowest desired temperature. This procedure simplified the setting of the thermoregulator, since the subsequent changes in temperature involved raising the bath temperature.

In order to show the laboratory arrangement of the cryostat and the attendant equipment, a photograph is presented in Fig. 3. As shown, the cryostat is being

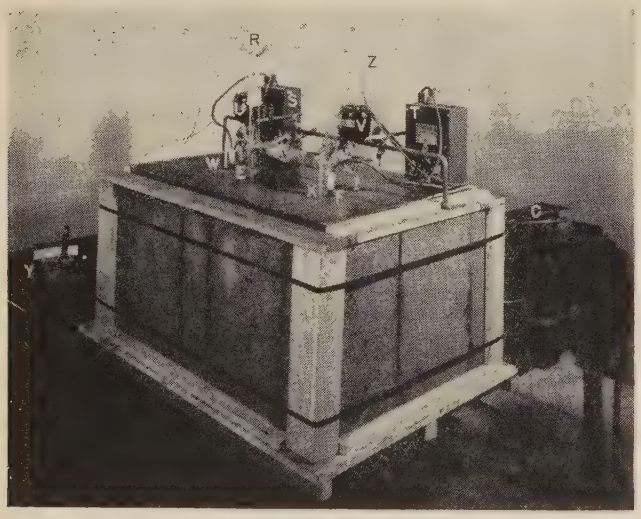


Fig. 3 Cryostat and auxiliary equipment

used for the calibration of an electric hygrometer. The thermoregulators e and f control the temperature of the two baths. They operate the on-off cycle of the knife type heaters through the relays s and t (Precision Scientific Co.). The stirrer motors that are mounted to a common bracket are shown at u and v and the thermometers are at w and x. The sealed-in electrical leads r at the upper left section of the humidity chamber m are connected externally to the meter y and internally to the electric hygrometers at s (Fig. 1). The vacuum pump used for evacuating the humidity chamber at z is located behind the cryostat and is not shown in the photograph. The 0.25-hp. refrigeration compressing unit is located to the right of the cryostat at c.

DESIGN OF APPARATUS FOR PERMEABILITY MEASUREMENTS AT LOW TEMPERATURES

A schematic diagram of the permeability testing chamber is shown in Fig. 4. This chamber is immersed in the left bath (k) of Fig. 1. The principle involved in this apparatus is essentially the same as that employed in the dynamic method at room temperatures. A test specimen (s) is sealed to the opening of a crystallizing dish (c) which contains a long, very fine capillary g for the purpose of equalizing the pressure between the dish and the outer atmosphere. Thus the pressure gradient across the test specimen is eliminated when the apparatus is taken from room temperatures and immersed in the low temperature bath. (The influence on relative humidity in the crystallizing dish (c) of water vapor diffusing through the capillary is negligible.) An inverted Petri dish containing an electric hygrometer (h) is sealed to the top of the specimen. A saturated salt solution is placed in the bottom of the crystallizing dish to condition the space below the specimen to a constant, high-relative humidity. The space above the specimen and that defined by the Petri dish is conditioned from an external source. Air from a compressed air line is passed through a capillary type flow meter, and through a drying tube containing Anhydrone into a coil of 0.5-inch copper tubing immersed in the right bath (l) of the cryostat, then through a coil of 0.25-inch copper tubing immersed in the left bath (k) of the cryostat, and finally into the inlet tube (a) and the space above the specimen. The air leaves the space through the tube b. The desired relative humidity of the air is obtained through the control of the temperature in the right bath. The inside of the larger copper coil is coated with a film of ice so that the air, on passing through the coil, is cooled and saturated with water vapor. As the air passes through the second coil in the left bath of the cryostat, it is warmed to the temperature of the bath before it enters the permeability apparatus. Thus, the air passing into the space above the specimen has a partial pressure of water vapor corresponding to the temperature of the right bath. The relative humidity is the ratio of the vapor pressures corresponding to the respective bath temperatures.

Slightly above the point where the inlet and outlet tubes enter the Petri dish, two small openings (l and m in Fig. 4) are provided in the walls of the tubes. The purpose of opening l is to direct a portion of the conditioned air into the space between the permeability test chamber and the outer vessel before and during a permeability measurement. By conditioning the outer space to a low relative humidity, the vapor-pressure gradient across the seal between the test specimen and the Petri dish is small and the effect of any possible leak is minimized.

The mercury valves (d and e) are used to seal the space above the specimen from the outside atmosphere while the rate of change of relative humidity in that space is being obtained. When in their lowered position, the mercury in the small iron vessels is below the end of the inlet and outlet tubes, thus permitting air

to pass through the intervening space. When the iron vessels are in the raised position, the mercury in them is forced into the tubes and closes off the flow of air, sealing the space above the specimen. The valves are

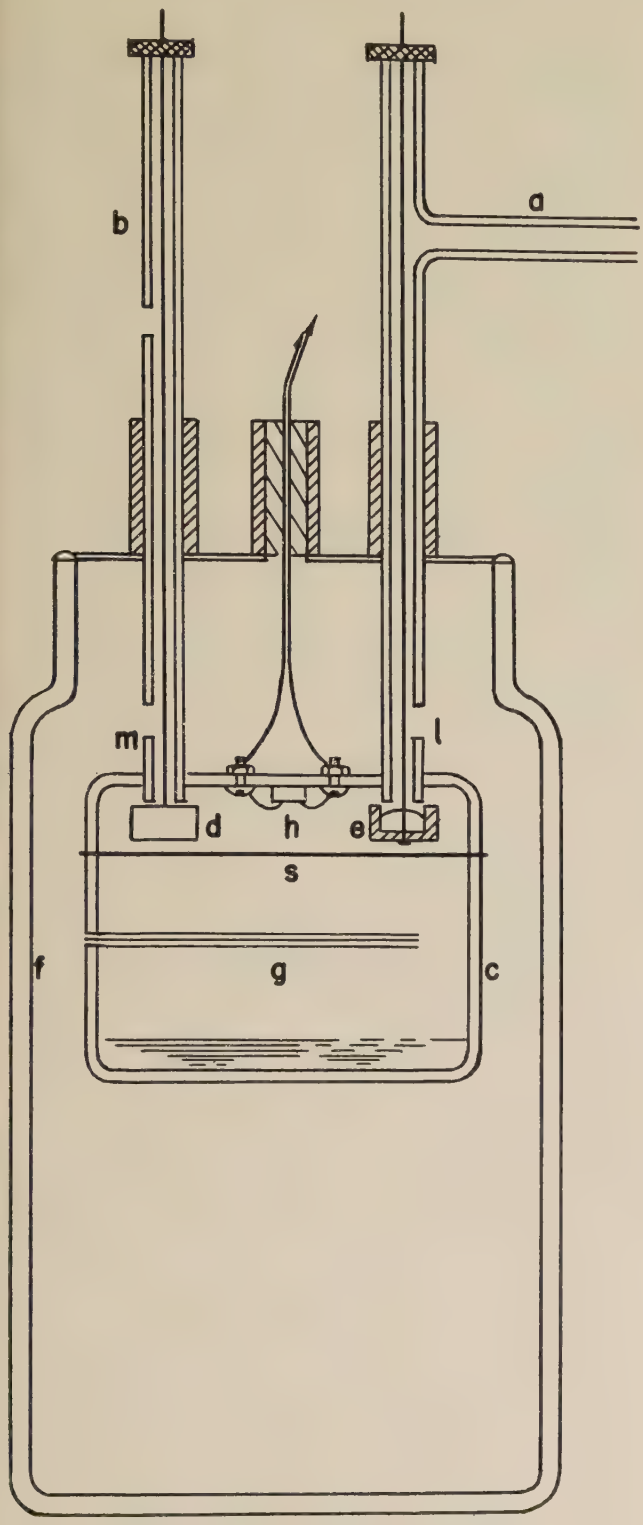


Fig. 4 WVP testing apparatus

held in any predetermined position by threaded rods and nuts at the top of the inlet and outlet tubes.

The outer vessel (f) of the permeability testing apparatus is a standard wide-mouth 1-quart Kerr canning jar. The cover of the jar is also a standard Kerr lid with the ordinary rubberlike gasket removed and replaced with a gasket made of Koroseal. Brass retainer cylinders are soldered to the lid at the point where the inlet and outlet tubes and the electrical connections for the hygrometer enter. The space between the glass tubes and the cylinders is filled with Wood's metal; that between the wire leads and the cylinder with wax. This type of cover permits immersion of the jar in the bath and prevents the alcohol from entering the jar. During experiments, the jar is submerged in the bath so that approximately 0.75 inch of the bath liquid covers the top. This is done to insure a constant uniform temperature of the apparatus in the jar.

CALIBRATION OF ELECTRIC HYGROMETERS AT LOW TEMPERATURES

The calibration of the electric hygrometers was performed in the humidity chamber m, which is shown schematically in Fig. 1. This chamber was constructed of 1.5-inch glass tubing and was equipped with ground-glass joints at n, o, and p, a stopcock at q, and sealed-in electrical leads (tungsten) at r. The electric hygrometer to be calibrated was suspended by the electrical leads near the bottom of the left tube of the chamber at s, and a small mound of flaked ice was placed on the bottom of the right tube of the chamber at t.

Since the distance between the mound of ice and the electric hygrometer is quite long, the chamber was connected to a vacuum pump at q and evacuated. The diffusion resistance of water vapor is appreciably less in a vacuum than it is in air at normal atmospheric pressures. While obtaining the calibration data, however, the stopcock q was closed.

The control of the relative humidity in the chamber depends on the temperature of the ice which is governed by the temperature of the right bath and by the ambient temperature of the electric hygrometer which, in turn, is governed by the temperature of the left bath. To obtain the relative humidity in the chamber, therefore, it is only necessary to observe the two temperatures, obtain the vapor pressures corresponding to these temperatures from handbook tables, and calculate the ratio. In this study, relative humidity is defined as the ratio of the actual water-vapor pressure in any space to the pressure of saturated water vapor at the same temperatures.

The calibration data obtained on four electric hygrometers at −18°C. are presented in Fig. 5. The moisture-sensitive coating of these hygrometers—namely, polyvinyl acetate (PVA) films—contained 1.0, 2.2, 3.0, and 4.0% of lithium chloride, respectively. The hygrometers were of the type described in Instrumentation studies LII (1). The polystyrene base of these hygrometers was approximately 2.5 inches long and an interval of approximately 2 inches of this distance was coated with the LiCl-PVA film. The calibration data appearing in Fig. 5 were obtained on the hygrometers after they had aged for a period of several weeks. The points represented by the solid dots were obtained for relative humidities approached from two directions —i.e., both from a high relative humidity and also from a low relative humidity. This was done to check the hygrometers for hysteresis effects at the reduced temperatures. The open circles for the hygrometers with

the 1.0 and 4.0% LiCl-PVA films represent the calibration values obtained after the hygrometers were alternately exposed to the low temperature and ordinary room temperatures. (In removing the hygrometers from a cold atmosphere, care was exercised to prevent

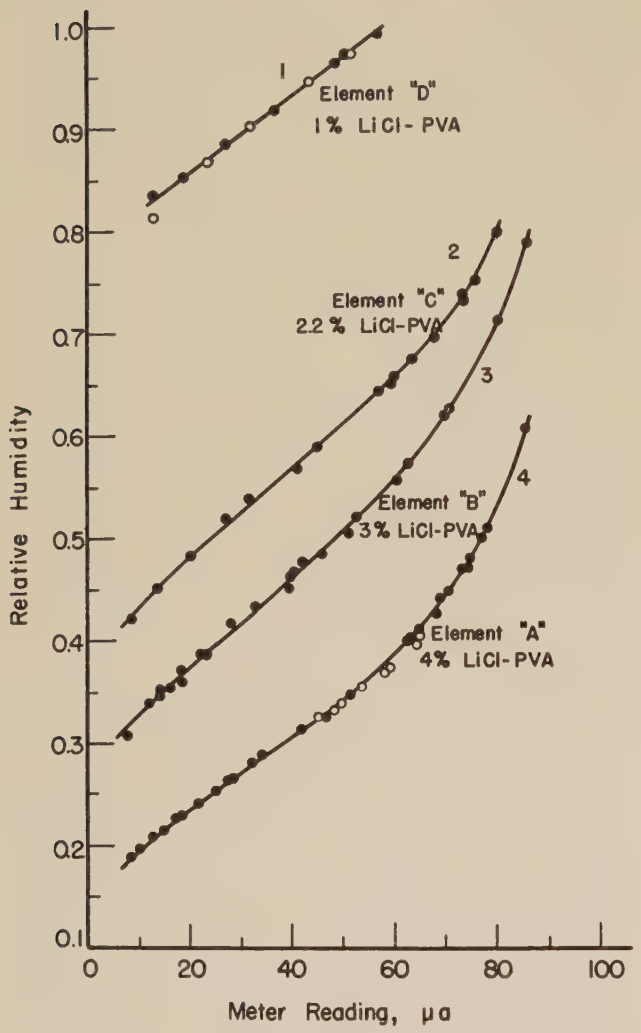


Fig. 5 Calibration curves for electric hygrometers at 0 °F

the condensation of moisture on the surface of the hygrometers.) In general, it may be stated that the electric hygrometers perform as well at the low temperatures as they do at normal room temperature.

EQUILIBRIUM RELATIVE HUMIDITIES ABOVE SATURATED SALT SOLUTIONS AT −18.0°C.

In order to establish as large a difference as possible in the partial pressures of water vapor at the two surfaces of the test specimen shown in Fig. 4, it was necessary to find a method for conditioning the space below the test specimen to a constant high relative humidity. Since saturated salt solutions had already been used for this purpose at normal room temperatures, the possibility of employing them at the low temperatures was investigated.

To determine the equilibrium relative humidity above the various saturated salt solutions, the humidity chamber (m, Fig. 1) in which the electric hygrometers were calibrated was employed. The chamber was separated at the ground glass joint o and only the left half of the chamber was used. A one-hole rubber stopper and a stopcock were fitted to the ground joint o to permit evacuation of the chamber before the equilibrium relative humidities were determined.

The saturated solutions of the various salts tested were prepared at room temperature and approximately 20 ml. of a solution, together with a small portion of the solid phase of the salt, were transferred to the bottom of the tube of the humidity chamber. Care was exercised in the transfer to avoid spilling the solution on the wall of the chamber. A glass spacer, a short test tube, and a calibrated electric hygrometer were then placed over the saturated solution. The electric hygrometer was inserted in the test tube which served to protect it against contamination by the salt. The chamber was connected to the vacuum pump and evacuated for approximately 15 to 30 minutes. At the end of this period, the stopcock in the vacuum line was closed and the hygrometer reading was observed periodically over an extended period of time or until equilibrium was obtained. The equilibrium relative humidity of the saturated salt solution was then obtained from the calibration chart of the electric hygrometer.

The equilibrium relative humidities over various saturated salt solutions, as determined by the foregoing method, are presented in Table I.

Table I. Relative Humidity over Saturated Salt Solutions at −18.0°C.

Chemical	*Formula*	*R.H., %*
Lithium chloride	LiCl	19.4
Sodium bromide	NaBr	84.5
Sodium nitrite	$NaNO_2$	87.2
Sodium chloride	NaCl	96.3
Potassium chromate	K_2CrO_4	100.0[a]
Ammonium su'phate	$(NH_4)_2SO_4$	100.0[a]

[a] These two values were beyond the calibration curve for the electric hygrometer and it was estimated that the relative humidity was very nearly 100.0%.

Of the solutions tested, it is believed that a saturated solution of sodium chloride is best suited for conditioning the space below the test specimen (Fig. 4). By controlling the relative humidity in the space below the test specimen at about 96%, two conditions are satisfied. (1) The high relative humidity permits the establishment of a large vapor-pressure gradient across the two surfaces of the specimen which is desirable in this study; and (2) the temperature change required to saturate the water vapor is sufficiently different from the normal variations in temperature of the cryostat that condensation difficulties should not occur.

DETERMINATION OF THE ABSORPTIVE CAPACITY OF THE ELECTRIC HYGROMETER AND GLASS

In obtaining water-vapor permeability data by the dynamic method, the permeability rates are established by determining the rate of increase of the relative humidity in a small space above the specimen. Factors governing these rates, in addition to the actual moisture transpiration of the specimen and the volume of the space above the specimen, are the absorptive and

adsorptive capacities of (1) the mass of the portion of the specimen lying above the moisture-resistant barrier, (2) the surface of the test enclosure, and (3) the electric hygrometer.

The first factor has been investigated and the results have been presented in Instrumentation Studies LIII (*2*).

The absorption of moisture by a surface or material in the test space reduces the rate of increase of the relative humidity in that space. Consequently, the true water-vapor permeability of the test specimen is not obtained from the dynamic rate unless the sorption characteristics of the materials exposed to the test space are known.

For the purpose of estimating the influence of the absorptive capacity of the hygrometer on the permeability data, a study was made of the variation of the moisture content of an electric hygrometer as a function of the relative humidity. The first part of this discussion deals with the absorption studies carried out at 73 and 100°F.; the results, therefore, are applicable to the dynamic method when it is used at normal room temperatures. The later part of this discussion deals with the absorption studies made at the lower temperatures. In the development of a method for obtaining the absorption data on the electric hygrometer at 73 and 100°F., the feasibility of employing the same method for the low-temperature absorption study was considered. Gravimetric methods for obtaining the absorption data at low temperatures were considered and rejected because it was believed that any method involving a weight determination would present problems which would be difficult to circumvent.

Accordingly, a method was developed in which the absorptive capacity of the electric hygrometer was obtained indirectly. In principle, this method involved the accurate measurement of a change of the relative humidity in a hermetically sealed vessel resulting only from a change in the temperature of the vessel. Based on this principle, the absorptive capacity of an electric hygrometer 2.5 inches in length and coated with a 4.0% LiCl-PVA film was obtained. The hygrometer, mounted on a piece of plate glass 5 inches square, was sealed over a Petri dish of known volume in a room conditioned at a relative humidity of 20% and a temperature of 100°F. This assembly was left in the conditioned room over an extended period of time to permit the establishment of equilibrium moisture conditions. The relative humidity as indicated by the hygrometer and the temperature at equilibrium were observed and recorded. Subsequently, the hygrometer assembly was transferred to a constant temperature room controlled at 73°F., where similar data were obtained. Following the establishment of equilibrium conditions at 73°F., the assembly was returned to the 100°F. room to check the original equilibrium values. A check of the original values served as an indication that no leaks had developed during the experiment. To permit the calculation of the absorptive capacity of the hygrometer, as based on the theory developed later in this report, the foregoing experiment was repeated, using a vessel of larger volume—e.g., a crystallizing dish instead of the Petri dish.

In the above experiment, the relative humidity values as obtained by the electric hygrometer include the adsorption of moisture by the glass surfaces as well as the absorption of moisture by the hygrometer. Consequently, in order to calculate the absorptive capacity of the electric hygrometer, it was first necessary to evaluate the adsorptive capacity of glass.

The adsorption data for glass were obtained gravimetrically on a Pyrex grade of glass wool. Glass wool was used to obtain these data because it is possible to carry out the weight measurements on a much larger surface area of glass than would have been possible by any other method. Approximately 2 grams of glass wool were placed in a vessel over phosphorus pentoxide and left in the dry atmosphere for a sufficient time to permit the establishment of equilibrium moisture conditions. Following careful weight determinations, the vessel containing the glass wool was transferred to an atmosphere conditioned at about 75% R.H., where the weight of the vessel of glass wool at equilibrium was obtained again. The apparatus used in obtaining these data was of such design that the weighing operation could be made without removing the glass wool from the conditioned atmosphere. The change in weight of the glass wool corresponding to a change in relative humidity of 75% was obtained at two temperatures—namely, 73 and 100°F.

After measuring the diameter of a large number of individual glass fibers (using a microscope equipped with a micrometer eyepiece), the surface area of the glass involved in the foregoing experiment was calculated from the following equation:

$$A = 4M\Sigma D_n/\rho\Sigma D_n^2,$$

where A is the total surface area of glass in square centimeters, M is the total mass of fibers in grams, ρ is the density of glass, ΣD_n is the sum of the diameters of the glass fibers measured in centimeters, and ΣD_n^2 is the sum of the squares of the diameters of the fibers measured in centimeters.

Based on data obtained in the above experiments, it was found that the adsorptive capacity of a glass surface at 73°F. was 3.55×10^{-7} gram per square centimeter per unit change of relative humidity, and at 100°F. it was 3.38×10^{-7} gram per square centimeter per unit change of relative humidity. The surface areas of the glass samples involved in the adsorption measurements at 73 and 100°F. were 3530 and 4120 square centimeters, respectively.

The hypothetical moisture absorption isotherms for an electric hygrometer, giving the moisture content as a function of the relative humidity, are shown in Fig. 6. The calculation of the moisture content of the hygrometer from the data obtained in the preceding experiments is based on the theory stated in the following equation. For a change in temperature from t_1 (100°F.) to t_2 (73°F.):

$$V_1\rho_1 = V_1\rho_2 + \Delta m_g + \Delta m_h, \qquad (1)$$

where V_1 is the volume of the vessel in which the change in relative humidity corresponding to the change in temperature from t_1 to t_2 was observed, ρ_1 is the density of water vapor in grams per cubic centimeter at t_1 for the relative humidity observed at t_1, ρ_2 is the density of water vapor in grams per cubic centimeter for the relative humidity observed at t_2, Δm_g is the mass of water vapor adsorbed by the glass surface of the vessel

resulting from the change in relative humidity in going from t_1 to t_2, and Δm_h is the mass of water vapor absorbed by the electric hygrometer resulting from the same change in relative humidity. Since the absorption data for the electric hygrometer were obtained as a result of a change in temperature from t_1 to t_2, the absorption of the hygrometer represented by Δm_h in equation (1) involves two quantities. Referring to Fig. 6, it is observed that

$$\Delta m_h = K\Delta r - m_o \qquad (2)$$

where m_o represents the change in the absorption characteristics of the hygrometer resulting only from the change in temperature t_1 to t_2, K is the moisture sorption per unit change in relative humidity at the lower temperature, and Δr is the change in relative humidity. Since two unknowns, m_o and K, are involved in the solution of the foregoing equations, the measurement involving the evaluation of the change in the relative humidity corresponding to t_1 and t_2 must be made on two different sized vessels.

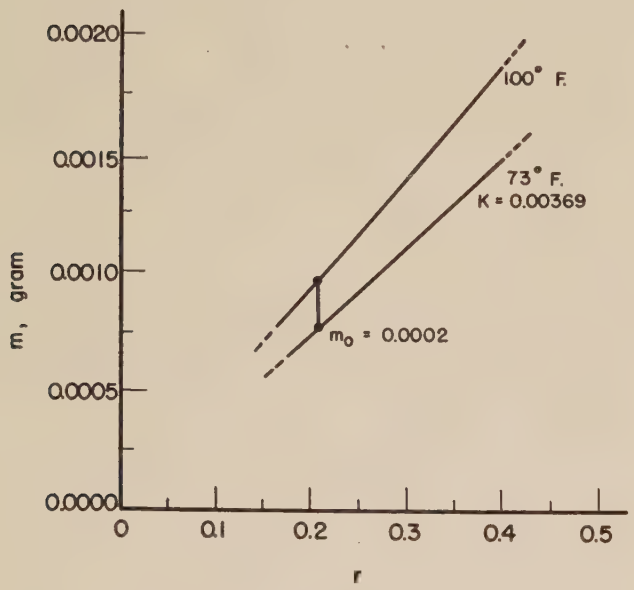


Fig. 6 Mass of water absorbed by hygrometer vs. relative humidity

The moisture adsorbed by the glass surfaces exposed to the test space in the dynamic method has an almost negligible effect on the permeability rates. For the glass surface involved in the dynamic test it was found that $K/A = 3.5 \times 10^{-7}$ gram per square centimeter, which is small when compared with the absorption of the hygrometer, for which $K/A = 7.8 \times 10^{-5}$ gram per square centimeter (A is the cross sectional area of the space above the specimen).

The absorption data of the electric hygrometer at the lower temperatures were obtained in the apparatus shown in Fig. 4. Essentially, the principle involved in obtaining the absorption data at the low temperature was the same as that used at the higher temperatures. In the apparatus shown in Fig. 4, the electric hygrometer was employed to measure the change in the relative humidity corresponding to a change in temperature from −12.2 to −18.0°C. for two vessels having different volumes. The smaller volume was obtained by sealing a flat piece of Pyrex glass over the opening of the Petri dish in the position normally occupied by the test specimen and the larger volume was obtained by sealing a crystallizing dish over the Petri dish. Both the flat glass disk and the crystallizing dish were sealed to the Petri dish with Celvacene and were held in their respective positions with a special spring clip which was supported by an inverted U-shaped metal band that fitted snuggly over the top of the Petri dish.

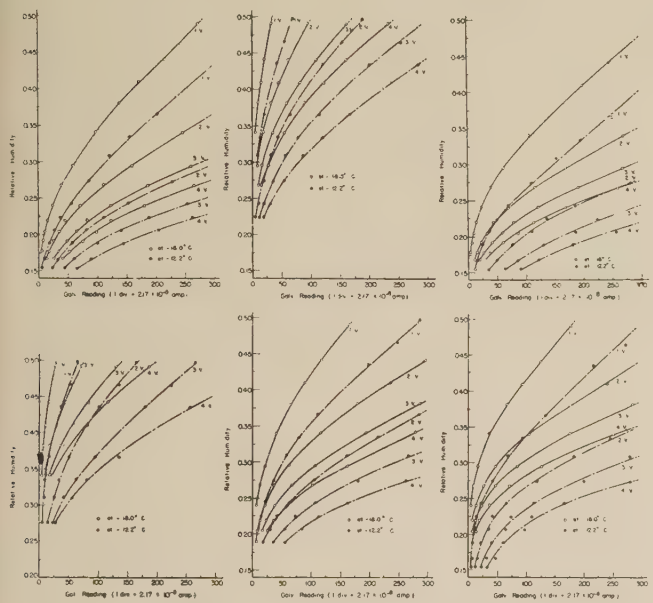
In obtaining the absorption data of the hygrometers with the apparatus shown in Fig. 4, precautionary measures had to be exercised. After sealing either the flat glass disk or the crystallizing dish to the open end of the Petri dish at normal room temperature, the mercury valves were opened and the assembly was placed in the constant temperature bath at −18.0°C. Having the valves in an open position while immersing the apparatus provided a means for equalizing the pressure between the vessel and the outer atmosphere and eliminated the danger of forcing mercury out of the valves. Following immersion of the apparatus in the low temperature bath, the air line was connected to the inlet tube of the Petri dish and the air, conditioned to a relative humidity of about 25% at −18.0°C., was passed into the space containing the hygrometer for a period of time (usually many hours) sufficient to establish constant temperature and relative humidity. When the relative humidity (as indicated by the hygrometer) was approximately the same as that calculated for the incoming air, the mercury valves were closed and the temperature of the bath was raised to −12.2°C. where, after equilibrium was established, the relative humidity and the temperature were observed and recorded. The temperature of the bath was subsequently lowered to −18.0°C. where again the temperature and relative humidity were observed and recorded after equilibrium was established. The foregoing cycle was repeated for the purpose of checking the data.

The first low temperature attempt to evaluate the absorptive capacity of an electric hygrometer, 2 inches in length containing a 4.0% LiCl-PVA film, was disappointing. The absorption of the hygrometer was so large that the relative humidity obtained at −18.0°C. was substantially the same as that obtained at −12.2°C. This served to indicate that an appreciable reduction in the absorption of the hygrometer was necessary before it could be employed successfully for evaluating water-vapor permeability rates at low temperatures.

DEVELOPMENT OF SMALL ELECTRIC HYGROMETERS

In order to reduce the absorptive capacity of the electric hygrometers, a study was undertaken of the performance of hygrometers on which an appreciable reduction was made in area of the moisture-sensitive film of LiCl-PVA. It was hoped that, by sensibly reducing the area of the LiCl-PVA film, a correspondingly large reduction in the absorptive capacity of the hygrometer would be obtained. Accordingly, several small hygrometers were made with the polystyrene base less than 0.25 inch in length and with the LiCl-PVA film confined to an area of approximately 2 sq. mm. This small spot of LiCl-PVA film was formed by dipping the end of a tapered, fire-polished glass rod

(end radius of curvature about 0.5 mm.) into the LiCl-PVA solution, and transferring to the groove of the hygrometer. In the first experiments on hygrometers containing a 4% LiCl-PVA film, it was found that the electrical resistance of the film was much higher than that encountered on the longer hygrometers and, as a result, the working range of the hygrometer was shifted from approximately 20 to 30% to 50 to 60% relative humidity. In view of these results, a series of hygrometers were prepared in which both the amount of lithium chloride in the PVA film and the width of the groove separating the two conducting surfaces of platinum were varied.



Figs. 7–12 Calibration curves for electric hygrometer

***Fig. 7* (0.023 in. groove, 6% LiCl-PVA, undiluted)**

***Fig. 8* (0.023 in. groove, 6% LiCl-PVA, diluted)**

***Fig. 9* (0.008 in. groove, 6% LiCl-PVA, undiluted)**

***Fig. 10* (0.008 in. groove, 6% LiCl-PVA, diluted**

***Fig. 11* (0.023 in. groove, 8% LiCl-PVA, diluted)**

***Fig. 12* (0.008 in. groove, 8% LiCl-PVA, diluted)**

Figures 7 through 12 present the calibration data obtained on this series of hygrometers. In each chart, the broken curve represents the data obtained at −12.2°C. and the solid curve represents those obtained at −18.0°C. It will be observed that, throughout the humidity range of interest, the calibration of the hygrometers was obtained at 4 different voltages—namely, at 1, 2, 3, and 4 volts as measured across the series combination of hygrometer, resistance, and galvanometer rectifier. In Figs. 7 and 8, a comparison is obtained between hygrometers having a diluted and an undiluted 6% LiCl-PVA film but the same groove width (0.023 inch). The diluted film for the work presented in this report refers to films obtained by diluting 1 part of the LiCl-PVA solution with 1 part of distilled water. In Figs. 9 and 10, data are presented for hygrometers having a diluted and an undiluted 6% LiCl-PVA film but a groove width of only 0.008 inch. For the data presented in Figs. 11 and 12, an 8% LiCl-PVA film (diluted) was used on hygrometers having groove widths of 0.023 and 0.008 inch, respectively.

In general, it will be observed that the concentration of the lithium chloride in the PVA film and the degree of dilution of the film had an appreciable effect on the electrical resistance of the hygrometers which is indicated by the range of relative humidities covered by a specific hygrometer. Of these two factors, the dilution of the PVA film accounted for a slightly larger shift in the range of relative humidities than did the change in concentration from a 6 to an 8% LiCl-PVA film. Least expected were the results obtained for the two groove widths, where it is noted that approximately the same result was obtained for groove widths of 0.023 and 0.008 inch.

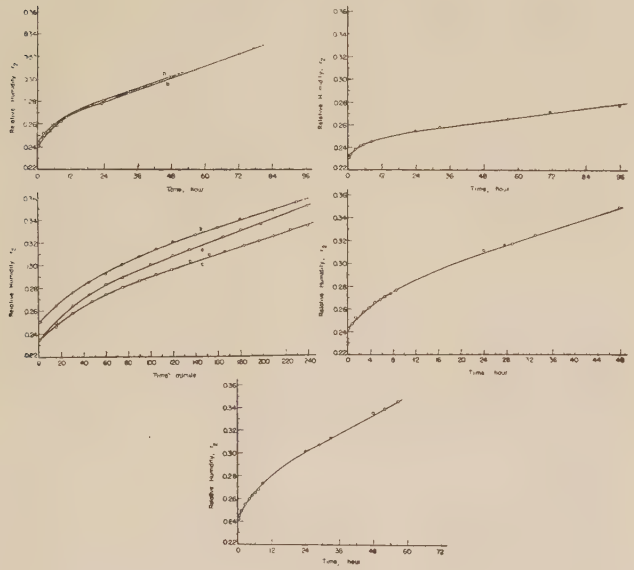
Absorption measurements were made for only one of the hygrometers described in the foregoing section. At a temperature of −18.1°C., a value of 0.0013 gram per unit change of relative humidity (0.000013 gram for 1% change in R.H.) was calculated for the absorptive capacity of an electric hygrometer containing a 6% LiCl-PVA film (undiluted). Since this value constituted a substantial decrease in the absorptive capacity of the electric hygrometers, the hygrometer containing the 6% LiCl-PVA film (undiluted) was subsequently employed to obtain the permeability data presented in the following section.

PERMEABILITY MEASUREMENTS WITH HYGROMETERS HAVING POLYSTYRENE BASE

The general procedure employed for obtaining permeability data with the dynamic method at a low temperature is the following: The permeability testing chamber, shown in Fig. 4, is removed from the Kerr jar and disassembled at room temperature. Approximately 20 ml. of a saturated salt solution (NaCl) having an equilibrium relative humidity of 96.3% is poured in the bottom of the crystallizing dish containing the fine long capillary. A thin film of Celvacene is applied uniformly to the ground edge of the crystallizing dish and the specimen to be tested is placed over the opening of the dish. The specimen need not be cut to the exact diameter of the crystallizing dish. In practice, it has been found desirable to cut the specimen considerably larger than the required size. This facilitates handling and eliminates the danger of contamination. After pressing the specimen into continuous contact with the film of Celvacene, another film of Celvacene is applied either to the top edge of the specimen or to the edge of the inverted Petri dish. The Petri dish containing the hygrometer is then placed over the specimen and crystallizing dish as shown in Fig. 4 and the special bracket and spring clip are attached to the assembly to support the crystallizing dish. The overhanging edge of the specimen is trimmed to the outer diameter of the crystallizing dish with a razor blade and the exposed edge of the specimen is covered with a layer of the Celvacene to prevent the transfer of water vapor through the edge of the specimen. Following assembly of the permeability testing chamber, a film of Silicone stopcock grease is applied to the upper edge of the Kerr jar, the permeability chamber containing the specimen is placed in the jar, and the screw type cover is turned up tight.

The mercury valves to the inlet and outlet tubes of the inverted Petri dish are subsequently opened and the sealed permeability apparatus is immersed in the left bath of the cryostat (Fig. 1). (For the permeability tests in this study, the temperature of the left bath was maintained at −18.1°C.) Opening the valves before immersing the test assembly in the low temperature bath is a necessary step in the procedure since this provides a means for equalizing the pressure between the test space and the outer atmosphere. A pressure difference across the specimen would cause the specimen to bow and subject it to undesirable stresses while the permeability tests were being made. Bowing of the specimen is also undesirable because the volume of the test space above the specimen would not be known.

The air line carrying the conditioned air is connected to the inlet tube of the Petri dish immediately after immersion of the assembly, so that, upon cooling, the alcohol vapors above the bath are prevented from being drawn into the test space above the specimen. The mercury valves are left in an open position so that the air which is conditioned to a known low relative humidity is permitted to pass over the specimen until the permeability test is started. Following a suitable conditioning period, the permeability test is started by closing the mercury valves to the inlet and outlet tubes of the Petri dish. The required permeability data are obtained by observing the hygrometer current as a function of the time and recording the observations.



Figs. 13–17 Increase of relative humidity with time

Fig. 13 (0.001-in Polythene) *Fig. 14 (0.002-in Polythene)*

Fig. 15 (75-gage Pliofilm) *Fig. 16 (140-gage Pliofilm)*

Fig. 17 (170-gage Pliofilm)

The dynamic permeability data obtained for two different samples of a moistureproof material are presented in Figs. 13 to 17 inclusive, where the relative humidity is plotted as a function of the time. Figures 13 and 14 present data for two samples of polythene having a caliper of 0.001 and 0.002 inch, respectively. The two curves appearing in Fig. 13 are for a single specimen of polythene obtained for different conditioning periods following immersion of the test assembly in the low temperature bath. The dynamic data for curve a were obtained 46 hours after immersion and those for curve b, 143 hours after immersion. The data for the polythene (0.002 inch) (Fig. 14) were obtained after a conditioning period of 16 hours.

Figures 15, 16, and 17 present the dynamic data for samples of 75, 140, and 170-gage pliofilm. Here, as for the polythene sample (0.001 inch), permeability data were obtained at different intervals of time following immersion of the specimen and test assembly in the low temperature bath. The three curves for the 75-gage pliofilm (Fig. 15), designated a, b, and c, were obtained for conditioning periods of 16, 39, and 88 hours, respectively. The data presented in Figs. 16 and 17 were obtained after conditioning periods of 48 and 24 hours, respectively.

Upon examining the permeability data presented in Figs. 13 to 17 inclusive, it will be seen that the permeability curves obtained at the low temperature are considerably different from those ordinarily obtained with the dynamic method at normal room temperature. (Typical permeability curves obtained at 73°F. are shown in Instrumentation Studies LII (*1*).) The significant difference between the dynamic data obtained at the two temperatures is that the permeability curves at the low temperature all exhibit a sharp inflection in the portion of the curve corresponding to relative humidities in the 24 to 28% range. These observed inflections constitute a departure from the type of permeability curve that should be obtained in measuring the rate of change of the relative humidity in the space above the specimen. When the difference in the relative humidity between the two surfaces of the specimen is as large as that obtaining for these permeability tests (0.73), the observed change in the relative humidity in the space above the specimen should be a relatively linear function of the time.

In an attempt to ascertain the reason for the observed shape of the curves, a number of factors concerning the operation of the permeability testing equipment were investigated. A leak or a temperature change in the space above the specimen, for example, could easily account for the observed departures from linearity. However, since there was no evidence to show that the observed inflections were caused by these factors, attention was drawn to the hygrometer itself.

In a further study of the hygrometers, two significant factors concerning the absorption characteristics of the polystyrene were revealed. (1) The polystyrene which is used as a base for the hygrometers accounts for nearly all of the absorptive capacity of the hygrometers. Gravimetric measurement (at room temperature) showed that the moisture adsorbed by a block of polystyrene was substantially the same as that adsorbed by a hygrometer of the same size containing a small spot of LiCl-PVA. (2) The equilibration rate of the polystyrene is slow. When a piece of the polystyrene in equilibrium with a known relative humidity was subjected to a change in relative humidity, from 4 to 7 days were required before a constant weight was again obtained and equilibrium re-established. This observed equilibration time, it would seem, is longer than should be required if the sorption of moisture by the polystyrene were strictly a surface phenomenon. The

adsorption of moisture in the microporous structure of the polystyrene apparently accounted for the slow rate of equilibration and the observed adsorptive capacity.

The foregoing sorption measurements led us to believe that the internal adsorption of moisture by the polystyrene was responsible for the observed inflections in the permeability curves obtained at the low temperature. Therefore, it was believed advisable to investigate the advantages of substituting other materials for the polystyrene in the hygrometers.

DEVELOPMENT OF HYGROMETER HAVING VYCOR BASE

Among the materials considered and subsequently employed as a substitute for the polystyrene in the base of the electric hygrometer were fused silica, glass, and Vycor (Corning Glass Works). Because of limited time, very little information on the performance of the hygrometers made of fused silica and glass has been obtained. However, a study of the Vycor hygrometer has been made and the permeability data obtained with it are presented in a latter section of this report.

Since the fused silica, glass, and Vycor are hard materials and could not be drilled and machined without special equipment, two essential changes were required in the method normally used in the fabrication of the polystyrene type of hygrometer. (The method for constructing the hygrometer of polystyrene is given in Instrumentation Studies LII (*1*).) The first of these changes involved the method for obtaining the gap in the platinum film so that two electrically insulated areas of platinum were obtained on the piece of Vycor. Formerly this gap was obtained by cutting a central groove on the hygrometer element after the polystyrene had been coated with a film of the platinum. On the Vycor base, this was accomplished simply by using a masking technique. The piece of Vycor, having been cut to the desired size, is cleaned thoroughly with water containing a wetting agent, then rinsed with distilled water, and air dried. Following this, it is placed on a flat metal plate, below a tight wire that has been drawn across the plate. The ends of the wire are anchored to the plate with screws. The piece of Vycor is positioned so that the wire passes over its center. It has been found that No. 18 gage copper wire has the proper diameter to give the desired gap in the platinum film. The platinum film is subsequently applied to the Vycor by the cathodic sputtering process.* During the sputtering operation, some platinum is deposited below the wire and on the edge of the Vycor. In those regions where such a deposit would electrically short the two adjacent halves of the platinum film, the platinum is removed by lightly grinding a short section of the edge with carborundum and water on a flat glass plate.

The second change involved the electrical connections to the platinum film. Since the Vycor could not be drilled and tapped, the electrical connections to the platinum film were made by using spring clips. The contacting arms of discarded electrical relays were found to be ideal for this purpose. One end of the spring clip rests directly on the platinum film, whereas the other is anchored below the terminal post (for example, the screw passing through the bottom of the Petri dish shown in Fig. 4).

The small spot of the LiCl-PVA film is applied to the gap between the two areas of platinum with a small tapered glass rod. The tip of the rod is merely dipped into a PVA solution containing the proper concentration of LiCl and a small amount of the solution is transferred to the hygrometer element.

Following the application of the LiCl-PVA film, the hygrometers were aged for approximately a week and then calibrated. The calibration curves presented in Fig. 18 were obtained for a Vycor hygrometer containing a 4% LiCl-PVA film. The solid curves represent

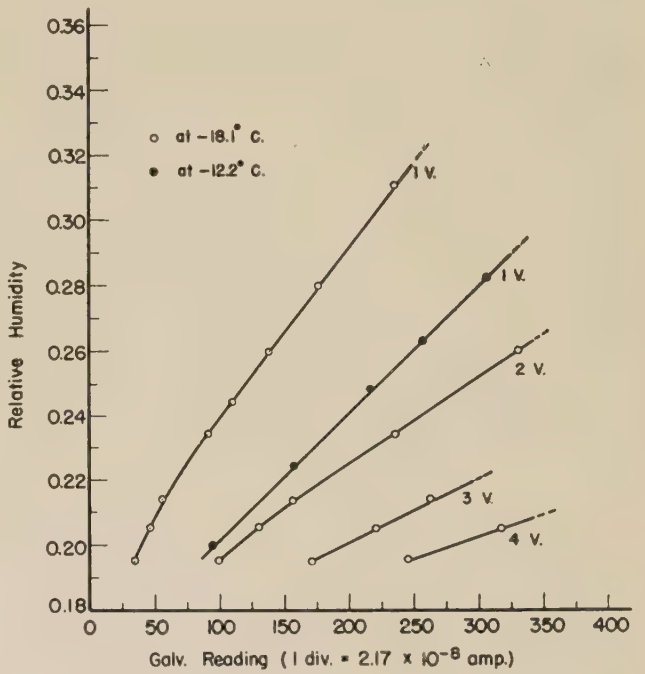
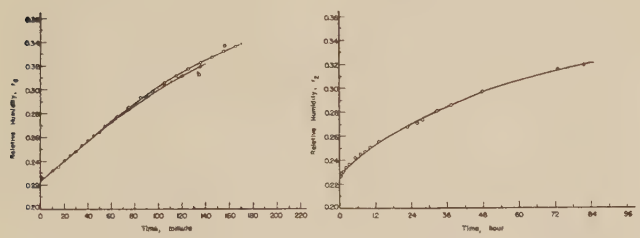


Fig. 18 Calibration curves for electric hygrometer with Vycor base (4% LiCl-PVA)

the data obtained at a temperature of −18.1°C. for 1, 2, 3, and 4 volts, respectively; the broken curve represents the data obtained at a temperature of −12.2°C. Upon examining the calibration data obtained for the differently constructed hygrometers, it will be observed that the sensitivity of the Vycor hygrometer is substantially the same as that observed for the polystyrene type of hygrometer (Figs. 7–12). The only essential difference between the two types of hygrometers is the LiCl concentration of the PVA required to cover a given range of relative humidity. The Vycor hygrometer with the 4% LiCl-PVA film covered approximately the same range of humidity as did the polystyrene hygrometer with the 6% LiCl-PVA film. This observed reduction in the concentration of the LiCl in the PVA is not attributed to the difference in the base stock of the hygrometers, but rather to the difference in the methods employed to obtain the gap in the platinum film. When the masking technique was employed in the fabrication of a polystyrene hygrometer, a similar reduction in the concentration of the LiCl had to be made in order to have the hygrometer cover the desired humidity range.

* The evaporative process would, of course, be suitable; in fact, because of its greater speed, the evaporative process would be preferred in commercial production of hygrometers.

The absorptive capacity for the Vycor hygrometer as calculated in accordance with the theory presented earlier in this report, is 0.0012 gram per unit change of relative humidity. Although this value is somewhat lower than that obtained for the absorptive capacity of the polystyrene hygrometer, it does not represent the improvement expected by substituting Vycor for the polystyrene as the base material of the hygrometers. It is surmised that, at the low temperature, where vapor pressure differentials are small and molecular activity is reduced, the inner portion of the polystyrene does not equilibrate to the surrounding moisture conditions in the time allotted to obtain the sorption data. In view of this consideration, the adsorption of moisture by the polystyrene at the low temperature would be primarily a surface phenomenon which could account for the fact that the observed absorptive capacity for the two hygrometers (Vycor and polystyrene) are approximately the same.



Figs. 19–20 Increase of relative humidity with time
Fig. 19 (75-gage Pliofilm) ***Fig. 20 (0.001-in. Polythene***

The permeability data obtained with the Vycor hygrometer containing the 4% LiCl-PVA film are presented in Figs. 19 and 20. The dynamic data presented in Fig. 19 are for a specimen of 75-gage pliofilm obtained for two different conditioning periods. The data for curve a were obtained after a conditioning period of 44 hours, whereas those for curve b were obtained after a conditioning period of 68 hours. The agreement between these curves, as judged by their initial slope, indicates that a constant rate of moisture transpiration had been attained by the time the first test was made.

The data presented in Fig. 20 are for a specimen of polythene (0.001 inch) obtained after a conditioning period of 89 hours.

In comparing the shape of the permeability curves obtained by the two different hygrometers, it will be observed that a substantial improvement has been made by substituting Vycor for polystyrene as a base material of the hygrometers.

CALCULATION OF PERMEABILITY RATES

Since the issuance of Instrumentation Studies LII (*1*) and LIII (*2*), a simplified method for calculating the water-vapor permeability from the dynamic data has been derived. The mathematical treatment leading to the simplification of the problem relies on the fact that, for moistureproof materials of low permeability, the diffusion resistance of the space above the specimen in the dynamic test is negligibly small in comparison with that of the barrier. On the basis of this assumption, the relative humidity differential across the barrier is $r_2 - r_1$. The rate of transmission of water vapor is then

$$\begin{aligned} PAp(r_2 - r_1) &= -\rho V\, dr_2/dt - dm_w/dt \\ &= -\rho V\, dr_2/dt - \Sigma K_i\, dr_2/dt \end{aligned} \qquad (1)$$

where the first term on the right side of the equation gives the rate of change of the moisture content of the space above the specimen and the second term gives the rate of absorption of material in the upper space. The latter term would include absorption of the hygrometer and all other materials exposed to the space above the moisture barrier.

Referring to the individual terms of equation 1, P is the permeability in grams per square centimeter per minute per unit vapor pressure differential across the specimen (in millimeters of Hg), p is the pressure of saturated water vapor, A is the area of the specimen, r_2 is the relative humidity in the space above the specimen, r_1 is the relative humidity below the specimen,* ρ is the density of saturated water vapor, V is the volume of the space above the specimen, and K_i is the mass of moisture sorbed by the ith object in the space above the moisture barrier per unit change in relative humidity (the specimen itself is, of course, included in the sum).

From equation (1), we obtain the simple first order equation.

$$dr_2/dt = -g(r_2 - r_1) \qquad (2)$$

where $g = pP/(\rho h + \Sigma K_i/A)$, in which h is the height of the space over the specimen (strictly, V/A). Integrating equation (2)

$$ln(r_2 - r_1) = -gt + \text{constant}$$

If we let r_3 designate the initial value of r_2 ($t = 0$), constant $= ln(r_3 - r_1)$. Substituting this value in the solution, we obtain

$$r_2 = r_1 + (r_3 - r_1)\, e^{-gt} \qquad (3)$$

In the present work, where dr_2/dt, the rate of change of the relative humidity in the space above the specimen is measured, the derivative of equation (3) is utilized. This is

$$dr_2/dt = g(r_1 - r_3)l^{-gt} \qquad (4)$$

If the rate of change of the relative humidity is calculated for $t = 0$, then equation (4) reduces to the following simple expression for the initial value:

$$(dr_2/dt)_0 = g(r_1 - r_3) \qquad (5)$$

To calculate the water-vapor permeability (WVP) from the dynamic data, dr_2/dt, in terms of units commonly used throughout the industry the following two equations are utilized:

$$P = (\rho h + \Sigma K_i/A)(dr_2/dt)_0/p(r_1 - r_3) \qquad (6)$$

and

$$\text{WVP} = 930000(r_1 - r_3)pP \qquad (7)$$

where the symbols have their previously defined meanings. Equation (7) gives the WVP in grams per 100 square inches per 24 hours for the given conditions of temperature and relative humidity differential across the specimen.

* The relative humidities r_1 and r_2 are *not* in per cent (for example, $r_2 = 0.50$ when the R.H. is 50%).

Although the foregoing treatment greatly simplifies the problem of calculating the water vapor permeability as derived from the dynamic data, it can be shown that this treatment agrees very closely with the more rigorous treatment of the problem presented earlier in Instrumentation Studies LII (*1*) and LIII (*2*).

RESULTS

Employing equations (6) and (7), the water-vapor permeabilities were calculated from the dynamic data for the samples of pliofilm and polythene that were obtained with the two different hygrometers. These data are presented in Table II, in which the first column designates the type of specimen used in the permeability test, the second designates the type of hygrometer, the third indicates the conditioning period, the fourth presents the dynamic data or the change of the relative humidity per minute and the fifth presents the calculated water-vapor permeability in grams per 100 square inches per 24 hours.

Table II. Permeability Data Obtained by Dynamic Method

(Conditions of Testing: Temperature = −18.1°C.; $r_1 = 0.96$; $r_3 = 0.23$)

Specimen	*Hygrometer type*	*Conditioning period, hr.*	*Dynamic rate, dr_2/dt ($\times 10^{-5}$)*	*Permeability, g./(100 sq. in./24 hr.)*
		Pliofilm		
75 gage	Polystyrene	16	101	0.0380
75 gage	Polystyrene	39	92	0.0347
75 gage	Polystyrene	88	78	0.0294
75 gage[a]	Polystyrene	24	74	0.0280
75 gage	Vycor	44	84	0.0298
75 gage	Vycor	68	84	0.0298
140 gage	Polystyrene	48	7	0.0026
170 gage	Polystyrene	24	10	0.0038
		Polythene		
0.001 in.	Polystyrene	46	8	0.0030
0.001 in.	Polystyrene	143	7	0.0026
0.001 in.[a]	Polystyrene	60	16	0.0060
0.001 in.	Vycor	41	7.5	0.0027
0.001 in.	Vycor	89	5.5	0.0020
0.002 in.	Polystyrene	16	4.5	0.0017

[a] Duplicate specimens.

The dynamic data giving the rate of change of relative humidity above the specimen were calculated for $t = 0$. To accomplish this, the original observations of the relative humidity and the time were plotted on linear chart paper using an expanded scale for the time axis (for example, like that of Fig. 19). In this way the slope of the initial portion of the permeability curve could be determined quite accurately. The testing time required to obtain sufficient permeability data to calculate the slope of the permeability curve is much shorter than that indicated by the curves presented in Figs. 13 to 17 and 19 and 20. When the data for the various samples are plotted on a chart having an expanded scale, it is observed that for the most impermeable specimen (0.002-inch.-polythene), a testing time of four hours is sufficient to define the slope of the permeability curve. By way of comparison, it will be observed in Fig. 19 that, for the specimen of 75-gage pliofilm, which had the highest permeability rate, a testing time of approximately 60 minutes is more than sufficient to establish the slope of the permeability curve at zero time.

Since no attempt had been made to evaluate the absorptive capacity of either the glass or the two samples (pliofilm and polythene) at the low temperature, estimated values of their absorptive capacity were utilized in calculating the permeability rates presented in Table II. In arriving at a value of $K = 4.0 \times 10^{-7}$ gram per sq. cm. per unit change of relative humidity as the estimated absorptive capacity for both the glass and the samples, it was assumed that (a) the absorptive capacity of the glass at the low temperature would be slightly higher than that observed at room temperature and (b) the homogeneous films of pliofilm and polythene which are considered moisture repellent or hydrophobic would have an absorptive capacity about the same as that of glass.

The permeability rates obtained for the different conditioning periods on the specimens of 75-gage pliofilm and 0.001-inch polythene tend to indicate that several days of conditioning are required before a constant rate of moisture transpiration is attained. The permeability data obtained with the polystyrene hygrometer on the specimen of 75-gage pliofilm would suggest that a conditioning period of more than 88 hours is required to establish a constant permeability rate, whereas those obtained with the Vycor hygrometer on another specimen of the 75-gage pliofilm indicate that a constant permeability rate had been attained for a condit oning period of 44 hours. The permeability data for the 0.001-inch polythene, obtained with both the polystyrene and the Vycor hygrometers, suggest that the conditioning period for the 0.001-inch polythene should be longer than that required by the 75-gage pliofilm. For both specimens of 0.001-inch polythene, it is observed that a constant permeability rate had not been attained for conditioning periods slightly over 40 hours.

If the permeability data for the 75-gage pliofilm and the 0.001-inch polythene are indicative of the conditioning time required to establish constant permeability rates, then it will be observed and could be concluded that the conditioning period for the remaining samples (the 140- and 170-gage pliofilm and the 0.002-inch polythene) were too short. Consequently, the observed permeability rates for these samples, as presented in Table II, are suspected of being somewhat high. It is unfortunate that the permeability data for the samples of 140- and 170-gage pliofilm and 0.002-inch polythene were not obtained for longer conditioning periods. When the original permeability measurements were made with the polystyrene hygrometer during the early phase of this study, too much attention was centered on the interpretation of the significance of the data above the knees of the curves. The observed parallelism in this portion of the curves for the different conditioning periods led us to the erroneous conclusion that a constant permeability rate had been attained.

The limited permeability measurements made with the polystyrene and the Vycor hygrometers indicate that the permeabilities as established with the two different hygrometers are in good agreement. Apparently, the internal adsorption of moisture by the polystyrene had a small effect, if any, on the initial slope of the permeability curves.

DISCUSSION

Permeability data have not been obtained, at the low

temperature, with the gravimetric method. Thus, a direct comparison of the dynamic and the gravimetric permeability data is not available for the reduced temperature. At room temperature, however, a comparison has been made of the permeability rates obtained with the two methods, employing one of the samples used for the low temperature study. Using the 170-gage pliofilm sample, it was found that, at 100°F., the agreement between the two different methods was well within 2%.

It should be emphasized that the dynamic method cannot be employed, at the low temperature, to measure permeabilities of a material having a high absorptive capacity. Because of the low density of saturated water vapor at the reduced temperature, the presence of an absorbing material, like cellulose, in the test space of the permeability chamber would seriously interfere with the test. The observed rate of change of relative humidity above such a specimen would be extremely small and the uncertainty involved in allowing for the absorption of the material lying above the vapor barrier could easily cause a serious error in the calculation of the permeability rates.

The amount of moisture adsorbed by glass depends not only upon its composition but also upon the treatment it receives following manufacture. Hence, care must be exercised in selecting the glassware that is to be used for the permeability chamber and for the absorption measurements of the electric hygrometers. Other observers (*3*) have observed that, when glass is subjected to corrosive cleaning agents, its adsorptive capacity increases appreciably. The adsorptive capacity of ordinary glass and Pyrex, for example, may increase by 100 to 200% and from 10 to 30%, respectively. A slight increase in the adsorptive capacity of glass is also observed when the glass is merely brought into contact with water. This observed increase in adsorption, however, is small compared with that obtained with the acid-treated glass. The glassware selected for the permeability chamber and for the absorption measurement of the hygrometers should be new unused Pyrex. Any necessary cleaning of this glassware should be done only with water containing a small amount of a good wetting agent.

STABILITY OF ELECTRIC HYGROMETERS

In studying the performance of the various hygrometers developed for application in the dynamic method, information on their stability (permanence of calibration) was also obtained and is presented for the benefit of those readers who are interested in using electric hygrometers of this general type. The hygrometers may logically be placed in three general classifications (these classifications apply only to those hygrometers having electrically insulated conductors which consist of platinum films; they do not apply to the wire wound type of hygrometer originally described by Dunmore). (1) Hygrometers having a polystyrene base on which the gap between the two adjacent areas of platinum is cut into the platinum film after the platinum is applied to the block of polystyrene. The LiCl-PVA coating on these hygrometers consists of a film which covers a $^3/_8$-inch or longer length of the gap. (2) Hygrometers similar to the above, except that the film of LiCl-PVA is confined to an area of approximately 2 sq. mm. (3) Hygrometers having a base of either polystyrene, Vycor, or glass, on which the gap between the two electrically insulated areas of platinum is obtained by the masking technique. The area of the LiCl-PVA film for these hygrometers is also confined to about 2 sq. mm.

In general, it was found that the stability of the large hygrometers falling in the first classification was good. With careful handling, it was observed that these hygrometers retained their original calibration for a period of at least 6 months.

The stability of the hygrometers in the second classification is inferior to that observed for the hygrometers of the other two classifications. At room temperature, the resistance of these hygrometers gradually increased with time and a shift in the calibration curve was observed. For a given hygrometer current (meter reading), this shift in the calibration curve, observed over a period of a week, represented a change in the relative humidity varying between 0.0 and 2.0%. When these hygrometers were used and stored at a low temperature, the observed stability over a 2-month period was satisfactory and no appreciable change in the calibration of the hygrometer was observed. It should be pointed out, however, that the observed instability of these hygrometers does not seriously impair their usefulness. The calibration of the hygrometers is easily checked by simply exposing them to the known equilibrium relative humidities of saturated salt solutions.

Since the hygrometers of the third classification were developed quite recently, information on their stability is meager. However, based on the information obtained thus far, it appears that the stability of these hygrometers will be superior to that observed for the hygrometers falling in the second classification.

CONCLUSIONS

It has been demonstrated that the dynamic method employing the electric hygrometer can be employed for evaluating the water-vapor permeability at reduced temperatures. The method can be employed only for measuring the permeability rates of materials having a low moisture absorptive capacity; the testing of a material having a high absorptive capacity would lead to complications and inaccuracy in calculating the permeability rates from the dynamic data. The chief advantage of the dynamic method lies in its speed. Following a suitable conditioning period, during which a constant rate of moisture transpiration of the test specimen is attained, permeability rates of the order of 0.001 gram per 100 square inches per 24 hours can be established in approximately a 4 to 5-hour period.

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- Fibrous Materials Testing Committee—E. R. Schafer, Forest Products Laboratory, Madison, Wis., Chairman.
- Nonfibrous Materials Testing Committee—J. P. Casey, New York State College of Forestry, Syracuse, N. Y., Chairman.
- Wax Testing Committee—A. M. Heald, Marathon Corp., Menasha, Wis., Chairman.
- Pulp Testing Committee—L. V. Forman, Institute of Paper Chemistry, Appleton, Wis., Chairman.
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- Microscopy Committee—C. E. Brandon, Aetna Paper Co., Dayton, Ohio, Chairman.
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- Chemical Methods Committee—Milton Fillius, Eastman Kodak Co., Chairman.
- Packaging Materials Testing Committee—L. E. Simerl, Marathon Corp., Menasha, Wis., Chairman.

Fifth Engineering Conference of the Pulp and Paper Industry. Netherland Plaza Hotel, Cincinnati, Ohio, October 2–5, 1950.
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- Data Sheets Committee—H. J. Perry, Lockwood Trade Journal Co., New York, N. Y., Chairman.

Plastics Conference. New York State College of Forestry, Syracuse, N. Y. October 19–20, 1950.

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